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Smart functionalized catalytic films for drinking water purification

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Problem statement

Problems regarding the need for clean water and the management of sanitation nowadays are of serious concern not only for third world countries, but also to other countries which are considered to have rich fresh water supplies. In an attempt to solve this fundamental problem, a lot of research and effort has been put into identifying new, robust methods of purifying water that are low cost, energy and time efficient and last but not least, minimise the chemical impact on the environment. This issue is crucial since it was reported that up till 2004, 1.2 billion people lack access to clean drinking water, and 2.6 billion have little or no sanitation. It is estimated that approximately 3,900 children die a day because of disease transmitted through contaminated water. In addition many more are sickened from diseases caused by waterborne bacteria and enteric viruses that have become a leading cause of malnutrition owing to poor digestion of the food eaten by people sickened by contaminated water\(^1,2\). Moreover, there is an increasing number of contaminants that continuously flow into the water supply annually. They range from common types of contaminants such as heavy metals to new emerging micropollutants such as endocrine disruptor compounds and nitrosamines. Due to this fact, there has been tremendous effort to develop more effective, low-cost and robust methods to disinfect and decontaminate water from the source to the point-of-use, without further stressing the environment or endangering human health by the treatment itself\(^3\).
Abstract

This thesis which is entitled “Smart functionalized catalytic films for drinking water purification” is a stepping stone towards overcoming this problem. This thesis evolved around designing new polymers that can be used to make membrane films which can anchor oxidation catalysts such as Fe-(TAML)s, concentrate pollutants and deliver hydrogen peroxide and base to the catalyst centres in a systematic and efficient way so that large volumes of water can be purified without having to contaminate the bulk water solution. In the first chapter green chemistry, oxidation chemistry, the use of hydrogen peroxide chemistry as an oxidant, and common contaminants found in wastewater are discussed, and in addition an overview of homogeneous and heterogeneous catalysts is given. In the second chapter details about the development of the special polymer that was used to form the smart catalytic films (SCFs) in this project is covered. In particular, details of how the polymer was formed, cast, cured, cross-linked and functionalized are discussed as well as the methods used to anchor the catalyst to the polymer film. Details of the mechanism by which the iron-TAML oxidation catalysts operate are presented since most of the subsequent studies involved the use of these compounds. Finally, preliminary studies of the performance of the SCFs in simple catalytic dye bleaching reactions are presented. These studies were carried out so that the most promising SCFs could be selected for further more detailed studies.

In the third chapter details of the more comprehensive tests carried out on the selected SCFs is covered. Catalytic oxidation experiments were carried out using water soluble organic dyes as surrogate pollutants with the smart catalytic film used in 3 different configurations; (i) simply suspended in solution in a beaker, (ii) as part of a “U-tube” device that uses the catalytic film to separate the hydrogen peroxide solution from the substrate (pollutant) solution and (iii) a “cross-flow” device that uses the catalytic film to separate the static hydrogen peroxide solution from the flowing substrate solution. In these three configurations the effects of changes to parameters such as pH, types of catalyst, catalyst loading and turbulent flow on the performance of the SCFs were investigated.

Finally, in chapter 4, the results of studies aimed at using the smart catalytic films to reduce or completely remove actual contaminants such as 17α-ethynylestradiol (EE₂), Bisphenol A (BPA) and Triclosan (TCS) are presented. In these studies the catalytic films were used in the three different configurations detailed above under the semi-optimized conditions that were discussed in chapter 3.
In the case of the studies with BPA and EE₂, some preliminary tests of the estrogenicity of the oxidation products formed after catalytic oxidative treatment with the SCFs were carried out using a yeast estrogen assay (YES) test to confirm that with the oxidative removal of these compounds from solution there was a corresponding drop in estrogenicity characteristics.
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*To have success, you can't let failure stop you. To have great success, you can't let success stop you*
Abbreviations

1. THM = trihalomethane
2. AOPs = Advanced Oxidation processes
3. PCDDs = polychlorinated dibenzodioxines
4. COD = carbon oxygen demand
5. EDCs = endocrine disrupting contaminants
6. DWTP = drinking water treatment plant
7. UF = ultra-filtration
8. RO = reverse osmosis
9. NF = nano filtration
10. MF = micro-filtration
11. NOM = natural organic matter
12. THMFP = trihalomethane formation potential
13. TFC = thin film composite
14. PA = polyamide
15. MA = methacrylic acid
16. SA = succinic acid
17. ED = ethylene diamine
18. WSC = water soluble carbodiimide
19. NHS = N-hydroxysuccinimide
20. BPA = Bisphenol A
21. Fe(III)-TsPc = Iron(III) tetrasulfophthalocyanine
22. TCS = triclosan
23. NADPH = nicotinamide adenine dinucleotide phosphate
24. POM = polyoxometallates
25. APOs = aluminophosphates
26. PACs = polyanionic chelating ligands
27. DCM = dichloromethane
28. TCP = 2,4,6- trichlorophenol
29. PCP = pentachlorophenol
30. CEC = compounds of emerging concern
31. PP = polypropylene
32. CMS = chloromethylstyrene
33. MWCO = molecular weight cut off
34. BPO = benzyl peroxide
35. CMSPs = chloromethylstyrene polymers
36. Tempo = 2, 2, 6, 6-tetramethyl-1-piperidinyloxy
37. TBC = tert-butyl catechol
38. AIBN = azobisisobutyronitrile
39. SDS = sodium dodecyl sulfate
40. DVB = divinylbenzene
41. MEK = methyl ethyl ketone
42. PDI = polydispersity index
43. PCMS = polychloromethylstyrene
44. DMF = dimethylformamide
45. PVdF-co-HFP = poly(vinylidene fluoride-co-hexa-fluoropropylene)
46. PVA = polyvinyl acetate
47. NMP = N-methylpyrrolidone
48. LCA = N,N-dimethylhexadecylamine
49. PE = polyester support
50. SF = smart film (film that already undergo functionalization, cross-linking and endcapping)
51. SCF = smart catalytic film (SF that anchored with oxidation catalysts)
52. THF = tetrahydrofuran
53. VOCs = volatile organic substance
54. HAAs = haloacetic acids
55. PAC = powder activated carbon
56. GAC = granular activated carbon
57. DOC = dissolved organic carbon
58. EE₂ = 17α-ethynylestradiol
Table of Contents

Problem statement ........................................................................................................... ii

Abstract .................................................................................................................................. iii

Acknowledgements ............................................................................................................. v

Abbreviation ......................................................................................................................... vi

List of Tables ......................................................................................................................... xviii

List of Figure .......................................................................................................................... xxiii

List of Equation ...................................................................................................................... xxxiii

Chapter 1 Introduction ........................................................................................................... 1

1.1 Introduction to Green Chemistry .................................................................................... 1

1.2 Oxidation Chemistry ....................................................................................................... 2

1.2.1 General comment about importance of oxidizing agents. ........................................ 2

1.2.2 Catalytic oxidation and Green Chemistry ................................................................. 3

1.2.3 Use of catalysis in Green Chemistry ......................................................................... 5

1.2.4 Focus on water purification, traditional ways to treat municipal water .................... 6

1.2.4.1 Mechanism for microconstituent removal by adsorption ...................................... 7

1.2.4.2 Powdered activated carbon vs granular activated carbon ..................................... 8

1.2.5 Advanced oxidation processes for water purification. .............................................. 9

1.2.5.1 Treatment with Ozone and Advanced Oxidation Treatment ............................... 11

1.2.5.2 Advantages and disadvantages of (AOPs) in general ........................................... 13

1.2.6 General EDC and Pharmaceuticals ............................................................................. 14

1.2.6.1 Method to remove EDCs and pharmaceuticals from drinking water .................... 18

1.2.6.1.1 UV-light based applications; UV/H₂O₂ and VUV ........................................... 19

1.2.6.1.2 Ozone based applications: O₃/H₂O₂, O₃/UV, O₃/H₂O₂/UV and O₃/H₂O₂/TiO₂ .......................................................... 19

1.2.6.1.3 Catalytic Oxidation ............................................................................................ 20

1.2.6.1.4 Fenton Processes ............................................................................................... 20

1.2.6.1.5 Miscellaneous treatment .................................................................................... 21
1.3 Hydrogen peroxide chemistry ................................................................. 26
   1.3.1 Hydrogen peroxide as an Oxidant .................................................. 26
   1.3.2 Physical and Chemical properties of Hydrogen Peroxide ..................... 29
   1.3.3 Fenton chemistry ............................................................................. 30
   1.3.4 Biological catalysts for H\textsubscript{2}O\textsubscript{2} oxidation reactions (peroxidases) ......................... 33
   1.3.5 Catalase destruction of hydrogen peroxide .......................................... 35
   1.3.6 other metal complex activation of hydrogen peroxide ......................... 37
      1.3.6.1 Metalloporphyrin ....................................................................... 40
      1.3.6.2 Biscyclam .................................................................................. 41
1.4 Homogenous and heterogeneous catalysis ................................................... 44
   1.4.1 Types of heterogeneous catalyst in general .......................................... 45
   1.4.2 Amino Groups Immobilized on Silica Gel: an Efficient and Reusable Heterogeneous Catalyst for the Knoevenagel Condensation ...................................................... 46
   1.4.3 Fabrication of hollow silica spheres with adsorbed Pd for Suzuki Coupling .... 49
   1.4.4 Supported Ruthenium Catalyst for the Heterogeneous Oxidation of Alcohols with Molecular Oxygen .............................................................................. 50
1.5 Catalyst Introduction .................................................................................. 52
   1.5.1 Design and Development of Fe-TAMLs catalyst .................................. 52
   1.5.2 Synthesis of Fe-TAMLs ..................................................................... 57
   1.5.3 Crystal Structure of Fe-TAMLs [Net\textsubscript{4}]\textsubscript{2}[FeB*(Cl)] catalysts ........................................ 60
   1.5.4 General properties of Fe-TAMLs ....................................................... 61
   1.5.5 Application of Fe-TAMLs in general .................................................. 62
      1.5.5.1 Degradation of environmentally persistent chemicals .................... 62
      1.5.5.2 Decolourization of Textile Effluent Streams .................................. 63
      1.5.5.3 Deactivation of persistent biological spores .................................... 64
      1.5.5.4 Pulp de-lignifications and wastewater effluent treatment ............... 65
   1.5.6 Evidence for the Fe\textsuperscript{V} oxidation state .................................... 68
   1.5.7 Proposed mechanism of action of Fe-TAMLs catalysts ......................... 68
1.5.8 Deducing rate law for the oxidation of substrates with the Fe³⁺-TAML/H₂O₂ system
........................................................................................................................................72
1.5.9 pH dependence of catalysis by Fe³⁺-TAMLs .................................................................74
1.5.10 Degradation of Fe-TAML catalyst .............................................................................75
2.1 CHAPTER 2 SUMMARY ......................................................................................................79
2.2 Description of the new oxidation system and how it works .............................................80
  2.2.1 Description of the technology .....................................................................................81
2.3 Smart polymer film formation ..........................................................................................83
  2.3.1 Different types of membrane technology .................................................................83
    2.3.1.1 Isotropic micro-porous membranes .....................................................................84
    2.3.1.2 Nonporous, Dense membranes ..........................................................................84
    2.3.1.3 Electrically charged membranes .........................................................................85
    2.3.1.4 Anisotropic membranes .....................................................................................85
2.4 Backing material used as membrane film support ............................................................86
2.5 Nanofiltration (NF) membranes .......................................................................................87
  2.5.1 Transport and selectivity models for NF and low MWCO UF membranes ...............89
  2.5.2 Advantages of membrane technology .......................................................................90
    2.5.2.1 Advantages of using NF membranes .................................................................90
  2.5.3 Factors affecting the performance of NF membranes ...............................................91
  2.5.4 Applications of NF membranes ...............................................................................92
    2.5.4.1 Use in polishing of conventional water treatment and wastewater treatment systems ........................................................................................................92
    2.5.4.2 Softening of seawater and brine solutions ............................................................92
    2.5.4.3 Dairies and –whey treatment ..............................................................................93
    2.5.4.4 Food Industry .....................................................................................................93
  2.5.5 Negatives features of using membrane filtration .......................................................93
2.6 General principles of the smart thin film can be summarized as below: .......................94
2.7 Traditional method to prepare Chloromethylstyrene polymer .........................................94
2.8 Different synthetic methods used to make polychloromethylenestrene

2.8.1 Homopolymerization of Chloromethylstyrene

2.8.2 Copolymerization of 50% styrene, 50% chloromethylstyrene

2.8.3 Emulsion polymerization of CMS

2.8.4 Images of PCMS formed by the solventless method

2.8.5 Images during emulsion polymerization

2.8.6 Images during Copolymerization reaction

2.8.7 Gel Permeation Chromatography GPC

2.8.7.1 How GPC work in general

2.8.7.2 Schematic of pore vs. analyte size

2.8.7.3 Summary of GPC results obtained

2.8.8 Examples of the construction of porous CMS (or other polymers) films on backing materials

2.8.9 Rheometer techniques to measure viscosity

2.8.9.1 Viscosity result batch 1 polymer

2.8.9.2 Viscosity result batch 2 polymers

2.8.10 Casting techniques

2.8.10.1 Dip coating

2.8.10.2 Spin Coating techniques

2.8.10.3 Flat spray process for optical coatings on cold glass

2.8.10.4 Doctor blade techniques

2.8.11 Summary of different methods of anchoring catalysts to solid supports

2.8.12 Functionalization

2.8.12.1 ATR-FTIR introduction
2.8.12.5 Introduction to scanning electron microscopy (SEM).................................132
2.8.12.5.1 SEM result top and on edge view ..........................................................133
2.8.12.6 TEM intro ..................................................................................................136
2.8.12.6.1 TEM result ............................................................................................137
2.8.12.7 Monitor surface area using Leica DMR research microscope (2 system)......139
2.8.12.8 Confocal laser microscope (CLM) ............................................................142
2.8.12.8 CLMS result Image of 50 µm thickness PCMS+ 0.5% DVB membrane immersed in ...........................................................................................................144

2.90 Anchoring the catalyst molecules on the smart films ....................................145

2.10 Choice of the best membranes for further study .............................................148
2.10.1 Preliminary test involving permeability with U-tube glass apparatus .........150
2.10.2 Preliminary tests involving bleaching with the catalytic polymer films ......151

2.11 Experimental procedures ..............................................................................161
2.11.1 Synthesis of the PCMS polymer using solvent ...........................................161
2.11.2 Synthesis of PCMS using no solvent ..........................................................161
2.11.3 Synthesis PCMS by emulsion polymerisation ............................................161
2.11.4 Syntheses of CMS/Styrene copolymers using (1:1 mole ratio of CMS: Styrene) using a solvent ........................................................................................................162
2.11.5 Synthesis of CMS/Styrene copolymers using (1:1 ratio of CMS: Styrene) using no solvent (i.e. homopolymerization) .................................................................162
2.11.6 Synthesis of PCMS polymer using toluene ...............................................162
2.11.7 Methods of casting the polymer on either polypropylene (PP) or polyester (PE) backing ...........................................................................................................163
2.11.7.1 Properties of selected backing membranes ............................................163
2.11.8 Curing procedures .......................................................................................164
2.11.9 Multiple coating procedures ......................................................................165
2.11.10 Typical GPC/Chromatogram procedures ................................................165
2.11.11 Typical method to functionalize Smart thin films

2.11.12 Rheometer to measure viscosity standard procedures

2.11.13 Method to use analyse samples with Leica DMR research microscope (2 systems)

2.11.14 Method for use of Andor Revolution spinning disc confocal laser microscopy

2.11.15 Method to use TEM

2.11.16 EDX-TEM normal cutting or cutting using a cryo-ultramicrotome

2.11.17 Method of sample preparation for SEM studies

3.1 Chapter 3 summary

3.2 Catalytic oxidation reactions in a Beaker

3.2.1 Thickness of the SCFs

3.2.2 Oxidation experiments carried out in beakers

3.2.3 Conclusions regarding the oxidations carried out using the beaker system

3.3 Catalytic oxidation experiments with a “U-tube” apparatus

3.3.1 Example of photos during experiments for (80:1) mole ratio of FeB*: Orange (II) pH 9.5x2

3.3.4 Conclusion for experiments conducted in the U-tube apparatus

3.4 Oxidation Experiments with the SCFs using a Cross-flow system

3.4.1 Large cross-flow

3.4.2 Conclusions for the Cross flow experiments

3.4.3 Experimental procedures

3.4.3.1 Preparation of solutions for standardization of thiosulfate and hydrogen peroxide

3.4.2.2 Preparation of 0.100 mol L⁻¹ Na₂S₂O₃ solution

3.4.2.3 Preparation of 2% w/v KI solution

3.4.2.4 Preparation of 1.00 mol L⁻¹ KI solution

3.4.2.5 Preparation of saturated ammonium molybdate, (NH₄)₆Mo₇O₂₄·4H₂O solution
3.4.2.6 Preparation of 1% w/v starch solution .................................................. 299
3.4.2.7 Preparation of 5x10^{-5} mol L^{-1} [Na]_2[FeB^\text{III}Cl] in buffer solution at pH ca 9.5 with 0.01 mol L^{-1} concentration ................................................................. 299
3.4.2.8 Preparation of 1.0 mmol L^{-1} orange (II) dye solution .......................... 300
3.4.2.9 Preparation of ca. 0.2 mol L^{-1} H_2O_2 solution .................................. 300
3.4.2.10 Preparation of 1% w/v starch solution ................................................. 300
3.4.2.11 Standardisation of 0.100 mol L^{-1} Na_2S_2O_3 solution ..................... 300
3.4.2.12 Standardisation of H_2O_2 solution ....................................................... 300
3.4.2.13 Standardisation of H_2O_2 using a UV-VIS instrument ....................... 301
3.4.2.14 Preparation of carbonate buffer (Na_2CO_3/ NaHCO_3) ..................... 301
3.4.2.15 Preparation of 0.1 mol L^{-1} Na_2CO_3 ................................................. 301
3.4.2.16 Preparation of 0.1 mol L^{-1} NaHCO_3 ................................................ 301
3.4.2.17 Purification of Orange (II) dye sodium ([4-[2-hydroxynaphthyl]-benzenesulfon ............................ 301
3.4.2.18 Diode Array UV-visible spectrometer ................................................ 302
3.4.2.19 Method used to prepare a standard calibration curve of rate of hydrogen peroxide bleaching of standard orange (II) solution vs concentration of (Na)_2[Fe^\text{III}(Cl)B^* (FeB^*)) ................................................................. 302
3.4.2.20 Preparation of orange (II) dye stock solution in carbonate buffer pH 9.5, temp 25 °C ................................................................................................................. 303
3.4.2.21 Method to investigate the permeation of carbonate buffer (0.01 M) through backing 2431 ND, 2471 and polyester backing .......................................................... 303
3.4.2.22 Method for obtaining calibration curve in homogenous system .......... 304
3.4.2.23 Typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored FeB* with (1:1) mole ratio .............................................. 304
3.4.2.24 Typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored ammonium molybdate tetrahydrate with (1:1) mole ratio ......... 305
3.4.2.25 Typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored sodium tungstate dihydrate with (1:1) mole ratio ............ 305
3.4.2.26 typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored FeB$^+(C_{16}H_{16}ClFeK_2N_4O_4)$ with (1:1) mole ratio ........................................ 306

3.4.2.27 Preparation of pinacyanol chloride stock solution ......................................................... 306

3.4.2.28 Preparation of safranine O stock solution ................................................................. 306

3.4.2.29 Preparation of phenolphthalein stock solution .......................................................... 306

3.4.2.30 typical bleaching experiment in U-tube system using orange II dye with a PCMS+NMP polymer and anchored FeB* with (1:1) mole ratio .................................................. 307

3.4.2.31 typical bleaching experiment in small cross flow system using orange II dye with a PCMS+NMP polymer and anchored FeB* with (1:1) mole ratio ........................................ 307

4.1 Summary to chapter 4 ........................................................................................................ 310

4.2 Introduction 17α-Ethynylestradiol ...................................................................................... 310

4.3 Introduction to Bisphenol A ............................................................................................. 311

4.3.1 Endocrine-disruptive effects of BPA on Aquatic Organisms ........................................ 314

4.4 Introduction to Triclosan ................................................................................................... 314

4.5 Mode of Action of Endocrine Disruptors .......................................................................... 315

4.5.1 Altered hormone synthesis ............................................................................................ 316

4.5.2 Altered hormone storage or release ............................................................................... 316

4.5.3 Altered hormone transport and clearance ..................................................................... 317

4.5.4 Altered hormone receptor recognition/binding ............................................................ 317

4.5.5 Altered Hormone Post-Receptor Activation ................................................................. 318

4.6 EE$\text{}_{2}$ oxidation with the FeB*/H$_2$O$_2$ homogenous system ............................................ 320

4.7 Oxidation of TCS and Bisphenol A with Fe-TAML/H$_2$O$_2$ in homogenous systems .... 320

4.8 Calibration curves for HPCL analysis of BPA, EE$_2$ and TCS ............................................ 321

4.8.1 Calibration curve for BPA .............................................................................................. 322

4.8.2 Calibration curve EE$_2$ .................................................................................................. 323

4.8.3 Calibration curve TCS .................................................................................................... 324

4.9 Reactions of BPA, EE$_2$ and TCS with SCFs in a beaker .................................................... 325

4.9.1 Oxidation Reactions of Bisphenol A (BPA) using the SCFs in a beaker .................... 325
4.9.2 Oxidation reactions of 17α-ethynylestradiol (EE₂) using the SCFs in a beaker .................................................. 328
4.9.3 Oxidation reactions of Triclosan (TCS) using the SCFs in a beaker ................................................................. 331
4.10 Oxidative removal of real-world pollutants catalysed by SCFs using a U-tube apparatus .................................................. 333
  4.10.1 Oxidation Reactions of BPA catalysed by SCFs in a U-tube apparatus .......................................................... 333
  4.10.2 Oxidation Reactions of EE₂ catalysed by SCFs in a U-tube apparatus ......................................................... 335
  4.10.3 Oxidation Reactions of TCS catalysed by SCFs in a U-tube apparatus ......................................................... 338
4.11 Oxidative removal of real-world pollutants catalysed by SCFs using a Cross-flow apparatus ........................................... 340
  4.11.1 Oxidative removal of BPA catalysed by SCFs using a cross-flow apparatus ................................................ 341
  4.11.2 Oxidative removal of EE₂ catalysed by SCFs using a cross-flow apparatus .................................................. 343
  4.11.3 Oxidative removal of TCS catalysed by SCFs using a cross-flow apparatus .................................................. 345
4.12 Yeast estrogen assay (YES) tests ....................................................................................................................... 348
4.1.3 Experimental Procedures ................................................................................................................................. 349
  4.1.3.1 Typical experiment involving oxidation of EE₂ by hydrogen peroxide catalysed by a SCF containing FeB⁺ in a beaker .................................................................................................................. 349
  4.1.3.2 Typical experiment involving oxidation of BPA by hydrogen peroxide catalysed by a SCF containing FeB⁺ in beaker .................................................................................................................. 350
  4.1.3.3 Typical experiment involving oxidation of TCS by hydrogen peroxide catalysed by a SCF containing FeB⁺ in beaker .................................................................................................................. 350
  4.1.3.4 Conditions for HPLC analysis of EE₂ ................................................................................................................. 350
  4.1.3.5 Conditions for HPLC analysis of BPA ................................................................................................................. 350
  4.1.3.6 Condition for HPLC analysis for TCS ................................................................................................................. 350
  4.1.3.7 Oxidative destruction of EE₂ with hydrogen peroxide using a SCF in the U-tube apparatus .................................................. 351
  4.1.3.8 Oxidative destruction of BPA with hydrogen peroxide using a SCF in the U-tube apparatus .................................................. 351
  4.1.3.9 Oxidative destruction of TCS with hydrogen peroxide using a SCF in the U-tube apparatus .................................................. 351
4.1.3.10 Oxidative destruction of orange (II), BPA and TCS with hydrogen peroxide using a SCF in the cross-flow apparatus

4.1.3.11 Procedure used to carry out the YES test on oxidatively treated EE₂ solution

4.1.3.12 Preparation of EE₂ stock solution

4.1.3.13 Preparation of BPA stock solution

4.1.3.14 Preparation of TCS stock solution

4.1.3.14 YES protocol

5.0 Conclusion
List of Tables

Table 1: Principles, advantages and disadvantages of GAC and PAC ........................................ 9
Table 2: Different Advanced Oxidation Processes ........................................................................ 10
Table 3: Contaminants in wastewater ....................................................................................... 15
Table 4: Bond Properties of H$_2$O$_2$ ...................................................................................... 29
Table 5: Substitution products of hydrogen peroxide ................................................................. 30
Table 6: Comparison between homogenous and heterogeneous catalysis ............................... 44
Table 7: Conditions used for oxidation of pulp and paper caustic waste water effluent ......... 65
Table 8: Condition used for optimum oxidation of caustic waste water effluent with second generation Fe-TAML complexes .................................................................................... 67
Table 9: Different type of polymerisation procedures ............................................................... 99
Table 10: Summarized GPC results for PCMS only and PCMS + 0.5% DVB after the TBC was removed ........................................................................................................................................ 106
Table 11: Summary of GPC results for PCMS only or with 0.5% Kraton or 0.5% BPO using solvent method without TBC being removed ........................................................................ 107
Table 12: Summary of GPC results for Copolymerization PCMS only or with 0.5% BPO using solvent method with TBC being removed ........................................................................ 108
Table 13: Functionalisation methods for the 7 best membranes .............................................. 125
Table 14: Standard bleaching condition .................................................................................... 145
Table 15: Bleaching run to measure leaching of Fe-(TAML) in buffer solution ................... 146
Table 16: Types of membranes that undergo permeability test ............................................. 149
Table 17: Summary of permeability experiment with u-tube .................................................. 150
Table 18: Summary of flow rate (mL/min) for respective smart films 100 µm thickness .... 150
Table 19: Summary of Flow rate (mL/min) for 3 best smart films nominally 250 µm thick 151
Table 20: Properties of polypropylene (PP) 2471 nd membrane .......................................... 163
Table 21: Properties of polyester (PE) backing membrane ..................................................... 164
Table 22: Conditions for the calibration curve of FeB$^*$ vs. initial rates of orange (II) oxidation ......................................................................................................................................... 173
Table 23: Conditions for the calibration curve of different [H$_2$O$_2$] vs. initial rates of orange (II) oxidation ........................................................................................................................................ 174
Table 24: Conditions for the calibration curve of the initial rate of Orange (II) oxidation vs. FeB$^*$ at pH 9.5. ............................................................................................................... 175
Table 25: Conditions for the calibration curve of the initial rate of Orange (II) oxidation vs. FeB$^*$ at pH 11.0. ............................................................................................................... 176
Table 26: Condition for first blank reaction .............................................................................. 177
Table 27: Condition for second blank reaction ....................................................................... 178
Table 28: Condition for third blank reaction ......................................................................... 180
Table 29: Condition to measure leaching reaction ................................................................. 181
Table 30: Summary bleaching reaction .................................................................................... 181
Table 31: Condition to measure leaching of catalyst ............................................................. 182
Table 32: Condition to measure catalase activity of the FeB* ........................................... 183
Table 33: Conditions to measure bleaching activity of FeB* .................................................. 186
Table 34: Conditions used to measure bleaching activity of the FeB* after exposure to 1.0 mM H₂O₂ .......................................................... 188
Table 35: Condition for bleaching reaction at pH 11 for 3 best SCF ..................................... 189
Table 36: Bleaching condition for 3 best SCFs at pH 11 ................................................. 192
Table 37: Bleaching condition for 3 best SCF at pH 6 ................................................... 195
Table 38: Bleaching condition for PCMS+NMP SCF with different stir rate at pH 9.5 201
Table 39: Bleaching condition for PCMS+NMP SCF (1:1) mole ratio of FeB*: PCl in homogenous system ................................................................. 197
Table 40: Condition of bleaching using PCMS+NMP (1:1) mole ratio with PCl at pH 9.5 198
Table 41: Condition of bleaching using (1:1) mole ratio FeB*: safranine O at pH 11 ...... 199
Table 42: Condition of bleaching using PCMS+NMP SCF (1:1) mole ratio with safranine O at pH 9.5 ................................................................. 201
Table 43: Condition of bleaching using PCMS+NMP SCF (140:1) mole ratio with safranine O at pH 9.5 ................................................................. 202
Table 44: Condition of bleaching using PCMS+NMP SCF (80:1) mole ratio with Orange (II) at pH 11 ................................................................. 204
Table 45: Condition of bleaching using PCMS+NMP SCF (80:1) mole ratio with Orange (II) at pH 9.5 ................................................................. 205
Table 46: Condition of bleaching using PCMS+NMP (80:1) mole ratio with Orange (II) at pH 9.5 with 0.01 mM H₂O₂ ........................................... 206
Table 47: Condition of bleaching using PCMS+NMP SCF mole ratio (1:1) to (100:1) with FeB²: Orange (II) at pH 9.5 with 1.0 mM H₂O₂ .................. 210
Table 48: Condition of bleaching using PCMS+NMP mole ratio (1:1) with FeB²: Orange (II) at pH 9.5 with 1mM H₂O₂ ........................................... 211
Table 49: Condition of bleaching using PCMS+NMP, PCSM+0.5% DVB, Copolymer +0.5% DVB mole ratio (1:1) with FeB²: Orange (II) at pH 11.0 with 1mM H₂O₂ ........................................... 215
Table 50: Condition of bleaching using PCMS+NMP SCF mole ratio (1:1) with FeB²: Orange (II) at pH 6.0 with 1.0 mM H₂O₂ ........................................... 219
Table 51: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with Ammonium molybdate: Orange (II) at pH 9.5 with 1mM H₂O₂ .................. 220
Table 52: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with ammonium molybdate: phenolphthalein at pH 10.5 with 1mM H₂O₂ in homogeneous system ........................................... 221
Table 53: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with ammonium molybdate: phenolphthalein at pH 10.5 with 1mM H₂O₂ on SCF in heterogeneous system ........................................... 222
Table 54: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with sodium tungstate: Orange II at pH 10.5 with 1mM H₂O₂ in homogeneous system ................................. 224
Table 55: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with sodium tungstate: phenolphthalein at pH 10.5 with 1mM H₂O₂ on SCF ........................................... 224
Table 56: Condition of bleaching using PCMS+NMP, mole ratio (10:1) with FeB*: phenolphthalein at pH 10.5 with 1mM H₂O₂ on SCF ........................................... 227
Table 57: bleaching condition in u-tube (1:1) mole ratio pH 9.5, 1.0 mM H₂O₂..........................234
Table 58: blank condition in u-tube pH 9.5, 1.0 mM H₂O₂.........................................................236
Table 59: blank condition in u-tube (1:1) mole ratio pH 9.5, 1.0 mM H₂O₂..........................236
Table 60: bleaching condition in u-tube (1:1) mole ratio pH 9.5 using stirring rate 1000 on Orange (II) side and 700 rpm on hydrogen peroxide side. ..........................................................237
Table 61: Bleaching condition in u-tube (20:1) mole ratio pH 7.1 using stirring rate 1000 on Orange (II) side and 700 rpm on hydrogen peroxide side. ..........................................................238
Table 62: Bleaching condition in u-tube (80:1) mole ratio pH 7.1 using stirring rate 1000 on Orange (II) side and 700 rpm on hydrogen peroxide side ..........................................................238
Table 63: bleaching condition in u-tube (80:1) mole ratio at various pH using stirring rate 1000 on both sides ........................................................................................................................................243
Table 64: bleaching condition in u-tube (140:1) mole ratio at various pH using stirring rate 1000 on both sides for 250 µm thickness ......................................................................................245
Table 65: The times taken for complete bleaching with the dye and hydrogen peroxide solutions at different pH values ..................................................................................................................245
Table 66: Bleaching condition in u-tube (140:1) mole ratio of FeB*: safranine O at various pH using stirring rate 1000 on both sides for 250 µm thickness ..........................................................249
Table 67: The times taken for complete bleaching with the dye and hydrogen peroxide solutions at different pH values ..................................................................................................................249
Table 68: bleaching condition in u-tube (10:1) mole ratio of (NH₄)₆Mo₇O₂₄·4H₂O): phenolphthalein at pH 10.5 both sides using stirring rate 1000 rpm on both sides ..........250
Table 69: Bleaching condition in u-tube (1:1) mole ratio of FeB⁺: pinacyanol chloride at various pH using stirring rate 1000 on both sides for 250 µm thickness ..........................................................252
Table 70: Bleaching condition in cross-flow (10:1) mole ratio of FeB*: Orange (II) at pH 9.5 x 10.5 at flow rate 1.0 mL/min with first generation mesh.................................265
Table 71: Bleaching result of first bleaching with first generation mesh .........................265
Table 72: Bleaching condition in cross-flow (10:1) mole ratio of FeB*: PCI with first generation mesh ......................................................................................................................................267
Table 73: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min .............................................................268
Table 74: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with first generation mesh ......................271
Table 75: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with second generation upside down ........272
Table 76: Bleaching condition in cross-flow (10:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with second generation .........................273
Table 77: Bleaching condition in cross-flow using (1:1) to (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with second generation mesh .........274
Table 78: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from 5.0 mL/min with second generation mesh with hydrogen peroxide reservoir 20.0 and 40.0 cm.........276
Table 79: Bleaching condition in cross-flow (80:1) mole ratio of FeB*: PCl with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm........................................................................................................278

Table 80: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCl with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm........................................................................................................279

Table 81: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCl with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm ..................................................................................................................................................280

Table 82: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm........................................................................................................282

Table 83: Bleaching condition in cross-flow (80:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm........................................................................................................283

Table 84: Bleaching condition in cross-flow (80:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with second and third generation mesh hydrogen peroxide reservoir 30.0 ........................................................................................................285

Table 85: Bleaching condition in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm.................................................................................................................286

Table 86: Bleaching condition in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm at pH 7x11..............................................................................................................287

Table 87: Bleaching condition in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm at pH 7x11..............................................................................................................288

Table 88: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm at pH 7x9.5.................................................................................................................290

Table 89: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.1 mM H₂O₂ at pH 7x9.5.................................................................................................................292

Table 90: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.01 mM H₂O₂ at pH 7x9.5.................................................................................................................293

Table 91: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.1 mM H₂O₂ at pH 7x8.0.................................................................................................................294

Table 92: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.01 mM H₂O₂ at pH 7 and pH 8.5.................................................................................................................295

Table 93: Physicochemical properties and estrogenic activity of EE₂ ..................................................................................................................311
Table 94: Condition for BPA calibration curve ................................................................. 322
Table 95: Condition for EE$^2$ calibration curve .............................................................. 323
Table 96: Condition for triclosan calibration curve ........................................................... 324
Table 97: Summarized BPA oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* ................................................................................................. 327
Table 98: Summarized BPA oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB$^3$ ................................................................................................. 327
Table 99: Summarized EE$^2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* ................................................................................................. 330
Table 100: Summarized EE$^2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB$^3$ ................................................................................................. 330
Table 101: Summarized TCS oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* ................................................................................................. 332
Table 102: Summarized TCS oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB$^3$ ................................................................................................. 332
Table 103: Summarized BPA oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* in u-tube system .................................................................................. 334
Table 104: Summary of EE$^2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* in u-tube apparatus ............................................................................. 337
Table 105: Summary of EE$^2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB$^3$ in u-tube apparatus ............................................................................. 337
Table 106: Summary of TCS oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* in u-tube apparatus ............................................................................. 339
Table 107: Summary of BPA oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* in small cross-flow apparatus ............................................................ 342
Table 108: Summary of EE$^2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* in small cross-flow apparatus ............................................................ 343
Table 109: Summary of TCS oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB* in small cross-flow apparatus ............................................................ 345
List of Figures

Figure 1: Traditional ways for water treatment ................................................................. 6
Figure 2: DDT on left and Octophenol on the right .......................................................... 16
Figure 3: Bisphenol A on the left and Methoxycchlor on the right .................................... 17
Figure 4: 17-α Ethynylestradiol on the left and 17β-Estradiol on the right ...................... 17
Figure 5: Bezafibrate on the left and Clofibrac acid on the right ....................................... 17
Figure 6: Carbamazepine on the left and Diclofenac on the right ...................................... 18
Figure 7: Primidone ............................................................................................................. 18
Figure 8: Schematic of membrane modification: (a) graft polymerization and (b) cross- linking of grafted polymer chains and substituting functional groups ................................ 22
Figure 9: Schematic diagram of nanofiltration system ....................................................... 23
Figure 10: Intermediates and by-products from the reaction of Fe(III) TsPC/H2O2 and a NF membrane .................................................................................................................... 24
Figure 11: Triclosan removal by laccase immobilized on mesoporous nanofibers: Strong adsorption and efficient degradation68 ............................................................. 26
Figure 12: Commercial preparation of hydrogen peroxide from auto-oxidation of 2-ethyl-9, 10-dihydroxlanthracene ..................................................................................... 27
Figure 13: Standard potential of redox reaction ................................................................... 29
Figure 14: Possible electro-Fenton reactions, reagent produced shown in bold .............. 32
Figure 15: Structure B ........................................................................................................ 35
Figure 16: Structure A ........................................................................................................ 35
Figure 17: Selected types of polyoxometallates ................................................................ 39
Figure 18: A chiral water soluble iron porphyrin .............................................................. 40
Figure 19: A tetraaza macrocyclic ligand referred to as biscyclam .................................... 41
Figure 20: Dinuclear-Mn–Me3tacn catalyst. Me3tacn=1,4,7-trimethyl-1,4,7 triazacyclononane .................................................................................................................. 42
Figure 21: Examples of Schiff-base ligands, which together with manganese have been patented as bleaching catalysts. ................................................................................... 43
Figure 22: Schematic representation of strategies for heterogenization of metal centre (M) .......................................................................................................................... 45
Figure 23: Catalyst system .................................................................................................. 46
Figure 24: Curved lines represent the surface of silica gel containing silanol groups and immobilized amino functions, dotted lines indicate breaking and forming bonds ............ 48
Figure 25: Suzuki Coupling reaction with iodothiphen and phenylboronic acid .............. 49
Figure 26: General oxidation of supported Ru catalyst with solvent ............................... 50
Figure 27: Oxidation of 2-octanol and 1-phenylethanol using Ru/Al2O3 in solvent free conditions .................................................................................................................. 51
Figure 28: Evolution of tetradequate ligand systems that, in general are progressively more suitable for supporting peroxide-activating catalysts ............................................. 53
Figure 29: Basic PAC ligand and complex structures ......................................................... 54
Figure 30: Diethyl Fe-TAML complex and its hydantoin degradation product..........................55
Figure 31: Hydrolytically stable di-fluorinated Fe-TAML complexes, [Fe(Cl)B*(F2)]− ..........56
Figure 32: General synthesis of the tetraamido macrocyclic ligand, TAMLs .........................58
Figure 33: Metallation of the tetraamido macrocycle with KOt-Bu and FeCl3 .......................59
Figure 34 : Crystal Structure of [NEt4][FeB*Cl2(H2O)]...................................................60
Figure 35: The organophosphorus pesticide fenitrothion ................................................62
Figure 36: Two examples of chlorophenols, TCP and PCP ............................................63
Figure 37: Fe-TAML complexes used to bleach pulp and paper caustic effluent waste water
.............................................................................................................................................67
Figure 38 : Speciation of [FeB*(Cl)]2- in aqueous solution..................................................69
Figure 39: Activation of the iron centre of the [FeB*(OH)2]2+ complex ...............................70
Figure 40: Overall catalytic cycle for [FeB*(Cl)]2- ................................................................71
Figure 41: Overall process for oxidation by FeIII-TAML catalysts ......................................72
Figure 42: Dependence of Kobs on pH, for the Fe-TAML catalyst [Fe(OH)2(B* Cl)]2- , conditions: [Fe-TAML]=1.28 x 10−7 mol L−1, [orange II]=5.81 x 10−5 mol L−1, and [H2O2]=3.3 x 10−4 mol L−1, in a 0.01 mol L−1 phosphate buffer..............................................................74
Figure 43: Mechanism of reactions of FeB* with peroxidases in water.................................75
Figure 44: Mechanism for one degradation pathway of activated of FeIII-TAML complexes 76
Figure 45: Phosphate-induced demetallation of Fe(III)-TAML complexes .........................77
Figure 46: Fe-TAML catalytic oxidation scheme ...............................................................80
Figure 47: Schematic diagram of the overall oxidation system that utilises Smart Catalytic Films (SCFs) .........................................................................................................................81
Figure 48: Schematic diagram of the principle types of membrane separated into two main types of membranes .................................................................84
Figure 49: Cross flow filtration flows parallel to the membrane .........................................87
Figure 50: Microfiltration retains the feed's suspended solids (left) and the UF separates macromolecules (right) ......................................................................................88
Figure 51: Reverse Osmosis membranes yield the cleanest permeate ................................88
Figure 52: The applicability ranges of different processes based on sizes ..........................89
Figure 53: Homopolymerization of Chloromethylstyrene ..................................................100
Figure 54: Copolymerization of styrene: chloromethylstyrene (1:1) mole ratio ..................100
Figure 55: Emulsion polymerization of CMS ........................................................................100
Figure 56: Thick layer of polymer after curing on a glass slide with pinholes .................101
Figure 57: Early experimental results using method A with Kraton G6932 on (left flask) and Kraton G6945 on (right flask) ..................................................................................101
Figure 58: LHS images of CMS washed with 0.5% NaOH, followed by deionized water wash in the middle and lastly CMS treated with K2CO3 (anhydrous) to remove remaining traces of water RHS ..............................................................102
Figure 59: Solvent method with inhibitor TBC being removed and heated in oil bath at 85°C for 5 hours under N2 atmosphere. LHS images of CMS washed with 0.5% NaOH, followed by deionized water wash in the middle and lastly CMS treated with K2CO3 (anhydrous) to remove remaining traces of water RHS .........................................................................102
Figure 60: Image 1 shows the solution containing deionised water, sodium lauryl sulfate, sodium hydrogen carbonate and potassium persulfate, image 2 after addition of CMS, methyl
acrylate and DVB, image 3 shows the emulsion polymer cooling in ice bath and finally image 4 shows the emulsion polymer after stirring for 5 hours. ................................................................. 103
Figure 61: Image 1 shows the mixture of CMS and styrene (1:1) mole ratio before heating, image 2 shows the viscous polymer formed, image 3 shows the addition of MEK while image 4 shows the formation of white flakes of polymer after precipitation.............................................. 104
Figure 62: Schematic representation of Molecular weight vs elution volume ............. 105
Figure 63: Plot of Shear rate against shear stress for 4 different polymers .................. 111
Figure 64: Plot of Shear rate against shear stress for six different polymers ............. 112
Figure 65: Fundamental stages of sol-gel dip coating (the finer arrows indicate the flow of air) ...................................................................................................................................... 113
Figure 66: Scheme of the Venjakob flat spray procedure ........................................ 115
Figure 67: Principle of doctor blading using a frame with a reservoir of coating liquid which is moving relatively to the substrate .................................................................................. 116
Figure 68: Wet layer thickness control by the gap between the frame and the blade ...... 116
Figure 69: Elcometer 4340 thin film applicator using a 4340 doctor blade ................. 117
Figure 70: slides cover with brown tap ........................................................................ 117
Figure 71: Actual images of sealing small scale (left) and actual sealing with big scale (right) ........................................................................................................................................... 118
Figure 72: Schematic diagram of the best sealing .......................................................... 118
Figure 73: LED lamp to measure pin holes .................................................................. 119
Figure 74: Simplified representation of multifunctionalized catalytic silica in hydrocarbon water mixtures ............................................................................................................. 121
Figure 75: Illustration of the supported solvent anchored liquid phase catalytic system ..... 121
Figure 76: Formation of novel silica-functionalized ammonium tungstate .................. 122
Figure 77: Silica xerogel covalently modified with phenyl groups and quaternary ammonium-poloxometalate (POM) ion pairs ................................................................. 123
Figure 78: (a) A representation of an FTIR spectrometer and (b) a representation of how the ATR principle works ........................................................................................................ 126
Figure 79: IR spectrum of PCMS without backing ....................................................... 127
Figure 80: IR chromatogram of PCMS with 2h quartenized with N,N-dimethylhexadecylamine and 1,4-dioxane in a (60:40) ratio ................................................................. 128
Figure 81: IR spectrum of PCMS with 5h quartenized with N,N-dimethylhexadecylamine and 1,4-dioxane (60:40) ratio ................................................................. 129
Figure 82: IR chromatogram of PCMS with 5h quartenized with N,N-dimethylhexadecylamine and 1,4-dioxane (60:40) ratio and 1,6- diaminohexane in 1,4-dioxane (60:40) ratio ................................................................. 130
Figure 83: IR chromatogram of PCMS with 5h quartenized with N,N-dimethylhexadecylamine and 1,4-dioxane (60:40) ratio and 1,6-diaminohexane in 1,4-dioxane (60:40) ratio and neat diethanolamine ................................................................. 131
Figure 84: Schematic diagram of a scanning electron microscope ................................ 132
Figure 85: SEM images of PCMS anchored with Orange (II) dye at 2 different spot on the same smart film (top view) .................................................................................. 133
Figure 86: SEM images of PCMS anchored with Orange (II) dye at 2 different spot on the same smart film (bottom view) .................................................................................. 134
Figure 114: Plot of initial rate of Orange (II) dye with different [H₂O₂] mM at pH 9.5
Figure 115: Plot of Initial rate of Orange (II) dye with different [FeB*] µM at pH 9.5
Figure 116: Plot of Initial rate of Orange (II) dye with different [FeB*] µM at pH 11.0
Figure 117: Plot of absorbance of Orange (II) dye with [H₂O₂] mM at pH 9.5
Figure 118: Plot of absorbance of Orange (II) dye with FeB* anchored on SCF without hydrogen peroxide at pH 9.5
Figure 119: Plot of absorbance of Orange (II) dye with FeB* anchored on SCF at pH 9.5
Figure 120: Plot of absorbance of Orange (II) dye with FeB* anchored on non-functionalised film at pH 9.5
Figure 121: Plot of Absorbance vs time for bleaching of Orange (II). SCF removed from solution at 4 minute and returned at 10 minute
Figure 122: Plot of initial rate of oxidation vs catalyst (FeB*) to dye mole ratio at pH 7
Figure 123: Plot of initial rate of oxidation vs catalyst (FeB*) to dye mole ratio at pH 9.5
Figure 124: Bleaching of Orange (II) using PCMS +NMP SCF
Figure 125: Bleaching of Orange (II) using PCMS + (0.5%) DVB SCF
Figure 126: Bleaching of Orange (II) after PCMS +NMP SCF immersed in H₂O₂
Figure 127: Bleaching of Orange (II) using PCMS + DVB (0.5%)
Figure 128: Bleaching of Orange (II) using Copolymer + DVB (0.5%) SCF
Figure 129: Bleaching of Orange (II) using PCMS + (0.5%) DVB SCF
Figure 130: Bleaching of 250 µm thickness PCMS +NMP SCF (140:1) mole ratio at pH 9.5
Figure 131: Bleaching of 250 µm thickness PCMS +NMP SCF (140:1) mole ratio at pH 11.0
Figure 132: Bleaching of 250 µm thickness PCMS +NMP (140:1) mole ratio at pH 9.5, SCF removed and returned 2 minutes later removed and returned 2 minutes later
Figure 133: Plot to measure leaching of FeB* using 250 µm thickness SCF (140:1) mole ratio, pH 9.50
Figure 134: Bleaching of 100 µm thickness PCMS +NMP SCF (60:1) mole ratio at pH 6.0
Figure 135: Bleaching using PCMS +NMP SCF (1:1) mole ratio pH 9.5 with different stirring speed
Figure 136: Bleaching (1:1) mole ratio of FeB*: PCl at pH 9.5 in homogeneous system
Figure 137: Bleaching of 250 µm thickness PCMS +NMP (1:1) mole ratio of FeB*: PCl at pH 9.5
Figure 138: Plot of bleaching for PCMS+NMP SCF (1:1) mole ratio at pH 11.0
Figure 139: Plot bleaching of PCMS +NMP SCF using safranine O, (1:1) mole ratio pH 9.5
Figure 140: Bleaching of PCMS +NMP SCF for safranine O (10:1) mole ratio, 100 µm thickness, pH 9.5
Figure 141: Bleaching for PCMS +NMP SCF (10:1) mole ratio pH 9.5 removed at 4 minute and returned back at 10 minute
Figure 142: Bleaching for PCMS +NMP SCF (10:1) mole ratio pH 9.5 removed at 4 minute and returned back at 10 minute
Figure 143: Bleaching for PCMS + NMP SCF (140:1) mole ratio in beaker with safranine O pH 9.5 ............................................................... 203
Figure 144: Bleaching for PCMS + NMP SCF (140:1) mole ratio in beaker with safranine O pH 11.0 ............................................................... 203
Figure 145: Bleaching for PCMS + NMP SCF (140:1) mole ratio pH 9.5 SCF removed at 3 minute and returned at 8 minutes later ................................. 204
Figure 146: Bleaching for PCMS + NMP, (80:1) mole ratio pH 11.0 in beaker with Orange (II) ................................................................. 205
Figure 147: Bleaching for PCMS + NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange (II), 0.1 mM H₂O₂ .......................................................... 206
Figure 148: Plot of bleaching using PCMS + NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange (II), 0.01 mM H₂O₂ ........................................... 207
Figure 149: Bleaching for PCMS + NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange II ........................................................................... 208
Figure 150: Bleaching for PCMS + NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange (II), exposed to 1.0 mM H₂O₂ ........................................... 208
Figure 151: Plot of initial rate of oxidation vs catalyst to dye mole ratio FeB⁺ pH 7 ............... 209
Figure 152: Plot of initial rate of oxidation vs catalyst loading for FeB²⁺ and FeB⁺⁺ at pH 9.5 .................................................................................. 210
Figure 153: Plot of absorbance vs time for PCMS + NMP SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 .............................................................. 212
Figure 154: Plot of absorbance vs time for PCMS + 0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 ............................................................... 212
Figure 155: Plot of absorbance vs time for Copolymer + 0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 Plot of absorbance vs time for PCMS+NMP SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 after exposure to hydrogen peroxide for 3hours .................................................. 213
Figure 156: Plot of absorbance vs time for Copolymer + 0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 ...................................................... 213
Figure 157: Plot of absorbance vs time for PCMS+NMP (0.5% DVB) SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 after exposure to hydrogen peroxide for 3hours .................................................. 214
Figure 158: Plot of absorbance vs time for Copolymer+0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 9.5 after exposure to hydrogen peroxide for 3hours .................................................. 214
Figure 159: Plot of absorbance vs time for PCMS +NMP SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 11.0 ........................................................................ 216
Figure 160 : Plot of absorbance vs time for PCMS +NMP SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 11.0 SCF removed and returned minute later ........................................... 216
Figure 161: Plot of absorbance vs time for PCMS +0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 11.0.............................................................. 217
Figure 162: Plot of absorbance vs time for PCMS +NMP SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 11.0 SCF removed from solution at 1 min and returned at 4 min .................................................. 217
Figure 163: Plot of absorbance vs time for Copolymer +0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 11.0 ........................................................................ 217
Figure 164: Plot of absorbance vs time for Copolymer +0.5% DVB SCF (1:1) mole ratio FeB⁺ ; Orange (II) at pH 11.0 SCF removed and returned 1.6 minutes later .................................................. 218
Figure 165: Bleaching for PCMS+NMP, (20:1) mole ratio pH 6.0 ........................................219
Figure 166: Plot of absorbance vs time for PCMS+NMP SCF (1:1) mole ratio ammonium molybdate: Orange (II) at pH 9.5.................................................................220
Figure 167: Plot of absorbance vs time for PCMS+NMP membrane (1:1) mole ratio ammonium molybdate: phenolphthalein at pH 10.5..............................................222
Figure 168: Plot of absorbance vs time for PCMS+NMP SCF (1:1) mole ratio ammonium molybdate: phenolphthalein at pH 10.5 with catalyst on the SCF....................................................223
Figure 169: Plot of absorbance vs time for PCMS+NMP (1:1) mole ratio ammonium molybdate: phenolphthalein at pH 10.5 after exposure to H₂O₂ for 1 hour...................223
Figure 170: Plot of absorbance vs time for PCMS+NMP membrane (1:1) mole ratio sodium tungstate dihydrate: Orange (II) at pH 10.5.........................................................225
Figure 171: Plot of absorbance vs time for PCMS+NMP membrane (1:1) mole ratio sodium tungstate: phenolphthalein at pH 10.5 .................................................................225
Figure 172: Plot of PCMS+NMP, (10:1) FeB*: phenolphthalein mole ratio pH 10.5 with 1.0 mM H₂O₂ .................................................................226
Figure 173: Plot of absorbance vs time for PCMS+NMP membrane (1:1) mole ratio sodium tungstate: phenolphthalein at pH 10.5, SCF removed from solution at 6 minute and returned back at 18 minute.................................226
Figure 174: schematic diagram of medium u-tube prototype........................................232
Figure 175: schematic diagram of medium u-tube prototype...........................................233
Figure 176: Image during experiments after overnight stirring........................................234
Figure 177: Plot of absorbance vs time for PCMS+NMP membrane without FeB* pH 9.5.235
Figure 178: Plot of absorbance vs time for (1:1) mole ratio pH 9.........................................235
Figure 179: Plot of absorbance vs time for PCMS+NMP membrane with FeB* without hydrogen peroxide .................................................................236
Figure 180: Plot of absorbance vs time for SCF (PCMS+NMP), pH 9.5 both sides with (1:1) mole ratio 1.0 mM H₂O₂ .................................................................237
Figure 181: Plot of initial rate vs different catalyst to dye mole ratio at pH 7.1, 1.0 mM H₂O₂ .................................................................239
Figure 182: Plot of absorbance vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H₂O₂ for different stirring speed.................................................................240
Figure 183: Plot of absorbance vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H₂O₂ for different stirring speed Plot of different stirring speed vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H₂O₂ .................................................................240
Figure 184: Plot of absorbance vs time for (80:1) mole ratio at pH 11.0, 1.0 mM H₂O₂ for different stirring speed.................................................................241
Figure 185: Plot of different stirring speed vs time for (80:1) mole ratio at pH 11.0, 1.0 mM H₂O₂ .................................................................241
Figure 186: Plot of absorbance vs time for (80:1) mole ratio at different pH combination, 1.0 mM H₂O₂ using 1000 rpm stirring speed.................................................................244
Figure 187: Plot of absorbance vs time for (140:1) mole ratio at different pH combination, 1.0 mM H₂O₂ using 1000 rpm stirring speed.................................................................246
Figure 188: Image 1 shows the initial colour of orange (II) dye at time zero, image 2 shows the colour of Orange (II) after 30 minutes, image 3 was taken after 60 minutes and image 4 was taken after 90 minutes.

Figure 189: Plot of absorbance vs time for (140:1) mole ratio at different pH combinations, 1.0 mM H₂O₂ using 1000 rpm stirring speed.

Figure 190: Plot of absorbance vs time for (10:1) mole ratio of (NH₄)₆Mo₇O₄⁴H₂O with flow rate from 1.0 to 10.0 mL/min with second generation mesh.

Figure 191: Plot of absorbance vs time for (1:1) mole ratio at different pH combinations, 1.0 mM H₂O₂ using 1000 rpm stirring speed.

Figure 192: Schematic diagram part by part in small cross-flow device.

Figure 193: Schematic diagram of small cross-flow.

Figure 194: Actual image of small cross-flow.

Figure 195: The whole set up including peristaltic pump and hydrogen peroxide reservoir.

Figure 196: Schematic diagram of the large cross-flow.

Figure 197: Peroxide support on the bottom reservoir.

Figure 198: Schematic diagram of the first generation mesh.

Figure 199: Actual picture of the first generation mesh.

Figure 200: Schematic diagram of the second generation mesh.

Figure 201: Schematic diagram of the third generation mesh.

Figure 202: Plot of absorbance vs flow rate for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min.

Figure 203: Plot of absorbance vs time for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with first generation mesh.

Figure 204: Plot of absorbance vs time for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with second generation mesh.

Figure 205: Plot of absorbance vs time for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with second generation mesh.

Figure 206: Plot of absorbance vs time for different range of mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with second generation mesh.

Figure 207: Plot of catalyst to dye mole ratio vs breakthrough flow rate point.

Figure 208: Plot of absorbance vs time for (140:1) mole ratio at pH 7x11, 1.0 mM H₂O₂ with flow rate from 5.0 mL/min with second generation mesh and hydrogen peroxide reservoir height (20-40) cm.

Figure 209: Plot of absorbance vs time for (80:1) mole ratio at pH 7 and 11, 1.0 mM H₂O₂ with flow rate from (1.0-10.0) mL/min with second generation mesh.

Figure 210: Bleaching condition in cross-flow (140:1) mole ratio of FeB⁺: PCl with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm.

Figure 211: Bleaching condition in cross-flow (140:1) mole ratio of FeB⁺: PCl with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm and 0.1 mM H₂O₂.

Figure 212: Bleaching condition in cross-flow (140:1) mole ratio of FeB⁺: PCl with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 40.0 cm and 0.1 mM H₂O₂.
Figure 213: Plot of bleaching in cross-flow (140:1) mole ratio of FeB: Orange II with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 40.0 cm and 0.1 mM H₂O₂..............................................................282
Figure 214: Plot of bleaching in cross-flow (80:1) mole ratio of FeB: Orange II with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................284
Figure 215: Plot of bleaching in cross-flow (80:1) mole ratio of FeB: Orange II with flow rate range from (1.0-10.0) mL/min with second and third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................285
Figure 216: Plot of bleaching in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................286
Figure 217: Plot of bleaching in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................287
Figure 218: Plot of bleaching in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................289
Figure 219: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................290
Figure 220: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂..............................................................291
Figure 221: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.1 mM H₂O₂..............................................................292
Figure 222: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.1 mM H₂O₂..............................................................293
Figure 223: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.1 mM H₂O₂ ..............................................................294
Figure 224: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.01 mM H₂O₂, at pH 7 and pH 8.5 ..............................................................295
Figure 225: Photograph of bleaching using small cross flow under condition specified in table 78 for the first 50 mL ..............................................................298
Figure 226: 17α-Ethynylestradiol ..............................................................310
Figure 227: Bisphenol A ......................................................................311
Figure 228: Chlorinated derivatives of BPA ........................................312
Figure 229: Chemical structure of TBBPA, tri-BBPA, di-BBPA and mono-BPA .....313
Figure 230: Triclosan ....................................................................314
Figure 231: mixture of the epimers 17α-ethynyl-1, 4-estradiene-10α,17β-diol-3-one .......320

xxxi
Figure 232: Calibration curve of BPA at 280 nm .................................................. 322
Figure 233: Calibration curve of EE₂ at 230 nm .................................................. 323
Figure 234: Calibration curve of triclosan at 280 nm .......................................... 324
Figure 235: Plot absorbance of Orange (II) with SF and 1.0 mM H₂O₂ .................. 340
Figure 236: Initial chromatogram of BPA 2ppm on the left and chromatogram of BPA remaining in exiting solution using condition entry 53 table 107 on the right .......... 342
Figure 237: Initial chromatogram of EE₂ 2ppm on the left and chromatogram of EE₂ remaining in exiting solution using condition entry 57 table 109 on the right .......... 344
Figure 238: Initial chromatogram of TCS 2ppm on the left and chromatogram of TCS remaining using condition entry 60 table 110 on the left .................................................. 346
Figure 239: YES test for EE₂ and BPA with E₂ as reference compound .............. 348
List of Equation

Equation 1: Production of active radical species .................................................. 12
Equation 2: pH dependent equilibrium of hydrogen peroxide .................................. 27
Equation 3: Base catalysed decomposition of hydrogen peroxide .............................. 28
Equation 4: Proposed steps in the mechanism for metal catalysed hydrogen peroxide decomposition ........................................................................................................ 28
Equation 5: Hydrogen Peroxide decomposition .......................................................... 30
Equation 6: Thermal Fenton and related reactions ..................................................... 31
Equation 7: Ligand to metal charge transfer excitation of Fe (III) complex ................. 31
Equation 8: Photolysis of hydrogen peroxide .............................................................. 32
Equation 9: Fenton reaction with hypochlorite as the oxidant .................................... 33
Equation 10: General reaction mechanism of peroxidases ......................................... 34
Equation 11: Classical catalytic peroxidation reaction .............................................. 34
Equation 12: Propose mechanism of action for Catalase ......................................... 36
Equation 13: General Knoevenagel reaction ............................................................. 47
Equation 14: Catalytic decomposition reaction of H₂O₂ ............................................ 68
Equation 15: Reactions for peroxidase action ........................................................... 69
Equation 16: Rate law for the oxidation of dye by hydrogen peroxide catalysed by FeIII-TAML .................................................................................................................. 72
Equation 17: Simplified rate law when the hydrogen peroxide concentration is low, so step I is rate limiting ................................................................................................. 73
Equation 18: Simplified rate law when hydrogen peroxide concentration is high, so step II is rate limiting ................................................................................................. 73
Equation 19: General scheme for Michealis Menten enzyme kinetics ....................... 73
Equation 20: Rate law for Michealis Menten enzyme kinetics ................................... 74
Equation 21: Calculation for k dependence on pH ..................................................... 75
Equation 22: Viscosity equation .................................................................................. 111
Equation 23: De Broglie Equation .............................................................................. 136
Chapter 1 Introduction

1.1 Introduction to Green Chemistry

In general, chemical processes involve substances that have the ability to cause harm to the environment. Hence, it is essential that chemists work to minimize the risks that are involved.

This risk can be explained as below:

\[
\text{Risk} = f(\text{Hazard, Exposure})
\]

Traditional methods have aimed to reduce the risk by limiting exposure. This was done by controlling factors such as handling, treatment, and disposal of chemicals. However, if these exposure controls fail, the consequences can be catastrophic. On the other hand, Green Chemistry works to reduce the risk by minimizing the hazard.Hazards can be defined as the ability of a substance to cause harm to humans or the environment. Reducing the hazard therefore, must occur in the design stages of a process.

Green Chemistry is defined as the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products. This concept was first formulated at the beginning of 1990s, and has led to the development of many green chemistry initiatives including the Green Chemistry Institute founded in 1990s, and the Green Chemistry Journal, which released its first issue in 1992.

The research surrounding Green Chemistry can be divided into three broad categories. The first is alternative feedstocks. One possibility is to use the waste from one process as a reagent in another process. A more drastic approach is to use only renewable or biologically derived feedstocks. Secondly, alternative solvents should be considered. This is because most reactions involve organic solvents. The best way to avoid problems with solvents is not to use solvents at all, however this is not plausible for all reactions and so supercritical fluids, water or ionic liquids maybe options. Finally alternative synthetic pathways should also be considered. It is often advantageous if these new pathways involve catalysts as these usually reduce energy input and increase selectivity.
1.2 Oxidation Chemistry

1.2.1 General comment about importance of oxidizing agents.

Oxidizing agents can be defined as elements or compounds in redox reactions that accept electron from another species. Examples of oxidizing agents that are widely used in industrial processes such as pulp and paper bleaching, laundry, water purification and textile dying are oxygen (O\textsubscript{2}), chlorine (Cl\textsubscript{2}) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}).

Oxygen is not often an oxidant on a lab scale but is more commonly used under pressure in industry. However, oxygen suffers from limitations such as high operation temperatures which can lead to an increase in capital cost and the possibility of explosions if not handled carefully. It also shows weak selectivity with respect to many other oxidation reactions\textsuperscript{7}.

On the other hand, hydrogen peroxide is a strong oxidizing agent that can be used to replace chlorine-based oxidants. The use of chlorine-based oxidants to oxidise organic material is undesirable due to the formation of toxic organo-chlorides side products, including dioxins. The advantage of using hydrogen peroxide is that in dilute solutions it is a relatively safe reagent with minimum toxicity to humans and it does not form organo-chlorides. However, upon exposure to heat it decomposes into oxygen and water which can lead to pressure build-up. The other main limitation hydrogen peroxide oxidations suffer from is that they are rarely selective because free radicals are usually involved\textsuperscript{8}. In addition, bleaching with hydrogen peroxide at significant rates normally requires high temperatures, pressures and longer reaction times which represent high costs for energy, equipment and labour\textsuperscript{8}.

In order to overcome these problems, a catalyst is needed. Using a catalyst lowers the activation energy needed for reaction and hence it also lowers the temperature and time required for oxidising organic compounds with hydrogen peroxide. This as a whole can add up to massive energy savings\textsuperscript{8}. The type of catalysts that were used in this study is discussed thoroughly in chapter 2.
1.2.2 Catalytic oxidation and Green Chemistry

These 12 principles of Green Chemistry were developed by Paul T. Anastas and John C. Werner as a guideline for past, present and future scientists to have better understanding regarding the scope of Green Chemistry in practice. The 12 principles are simply summarized as below:

1. Prevention of waste
2. Atom Economy
3. Minimize use and generation of hazardous substances
4. Designing safer chemicals
5. Designing safer auxiliary substances
6. Maximizing energy efficiency
7. Used renewable feedstock
8. Minimize usage of derivatization
9. Designing superior catalytic reagents
10. Designing degradable chemical products
11. Real time analysis pollution prevention
12. Minimize risk of accident

The first principle is the prevention of waste wherever possible. This principle has become a major concern especially in the past twenty or thirty years since the cost of treatment and disposal of chemical substances have increased. This is true regardless of whether the research is done on a large industrial scale or in small academic laboratories. A common waste is the starting material or reagent that is unconverted to products. Waste can be in any form and will impact the environment depending on its nature, toxicity, quantity and method of release.

The second principle evolved is regard to atom economy. This is a crucial tool to evaluate how well the starting materials are being incorporated and used to generate the final product. In other words, the synthetic pathway is said to be 100% atom economical if atoms of the reactants are incorporated into the product completely.

Thirdly wherever possible, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment. By
designing chemistry that reduces or eliminates hazards, all problems such as high cost, restrictive laws and bad perception of the scientific community can be avoided.

The fourth principle involves the design of safer chemicals. This can only be achieved if the right balance is maintained between maximizing the desired performance and function of the chemical product while ensuring the toxicity and hazard is reduced to its lowest level\(^4\).

Minimizing or preventing the use of auxiliary substances is also an important consideration. This is because most of the auxiliary chemicals used, such as halogenated solvents and volatile organic substance (VOCs) are coupled with health hazards including being suspected human carcinogens\(^9\).

The sixth principle involves energy efficiency where requirements should be recognized for their environmental and economic impacts and should be minimized\(^9\). This principle can be implemented in several ways. For instance, catalysts can be used to lower the activation energy of reactions and hence speed up the reactions. In addition, microwave techniques can also be implemented which show significant advantages in reducing prolonged heating for particular reaction\(^9\). In addition, it is crucial that methods use renewable energy resources rather that depleting the world’s fossil carbon fuel supply\(^1\). The feedstock would be best originated from renewable resources which are often associated with biological and plant-based starting materials\(^9\). Moreover this principles also concerns the avoidance where possible of unnecessary derivatization (blocking groups, protection/ deprotection, temporary modification of physical/chemical processes)\(^9\).

Usage of catalytic reagents which are superior to stoichiometric reagents is important in chemistry. Use of a catalyst can selectively enhance production of specific products, minimize energy usage and cost.

Furthermore, the product formed should be designed to breakdown and not to persist in the environment\(^9\). This is crucial because once chemicals are released into the environment, persistent chemicals will remain in the same and can be taken up into various plant and animal species which could accumulate in their systems and often be detrimental to the species\(^9\).

Analytical processes, especially those that enable reactions to be monitored in real time, can play an important role in the control of reactions which in turn leads to the minimisation of side-products and waste. Analytical chemistry is also used to monitor the formation of waste
and toxic by-products from any process so that the impact of the process on the environment can be measured\textsuperscript{11}

Last but not least is the principle of minimizing the risk of chemical accidents, including the release of chemicals, explosions and fires\textsuperscript{9}. This can be done for instance by replacing volatile liquids with solids or low vapour pressure substances. Other approaches include avoiding the storage of large amounts of harmful materials if these must be used (i.e. “just in time” operational procedures) \textsuperscript{9}.

1.2.3 Use of catalysis in Green Chemistry
Catalysis has made significant progress over the last twenty years. Catalysts work by interacting with starting materials to lower the activation energy of a reaction\textsuperscript{12}. Through lowering the activation energy, catalysts will increase the rate of the reaction, as well as decrease the energy requirements\textsuperscript{12}. When a catalyst is designed, three main factors are considered. First selectivity, which is the amount of substrate converted to the desired product. Next is the turnover frequency; this is the number of moles of product produced per second. Finally the turnover number, which is the amount of product formed per mole of catalyst\textsuperscript{12}. Other characteristics that need to be considered are stability, solubility, and the ease of separation from the product\textsuperscript{4}.

Catalysts offer numerous benefits in terms of green chemistry. Obviously, they are included in principle nine; however catalysis can be used to achieve many of the other twelve principles. For example, by driving the reaction to the preferred product, catalysts are able to reduce by-product formation and therefore minimize waste\textsuperscript{4}. They also lower the energy costs of a reaction, can decrease the need for processing and separation agents, and allow the use of less toxic starting materials. Heterogeneous catalysts provide an additional advantage as they eliminate the need for separation procedures such as extraction\textsuperscript{4}. Fortunately, catalysts also provide economic benefits, which is a central driver to the advancement of green chemistry.
1.2.4 Focus on water purification, traditional ways to treat municipal water

Water is a major component in human life. We use it daily for cooking, drinking, showering and washing. Fresh drinking water is a basic necessity for the maintenance of good health in humans, but it is also a vehicle for the introduction of harmful compounds and biological agents such as bacterial and protozoan pathogens into the body\textsuperscript{13}. Thus purifying water from sources such as surface water supplies and groundwater is crucial to ensure they are safe to drink. Industrial processes for water purification involve numerous steps including the following: pre-treatment (pre-coagulation, pre-disinfection), aeration, coagulation, filtration (slow, rapid, ultra-filtration, carbon filtration), disinfection (chloramines, ozonation, ultraviolet light, chlorination) and miscellaneous treatments (Fe/Mn removal, deionization, reverse osmosis, algal/odor control, softening, ion-exchange, fluoridation and radioactivity removal)\textsuperscript{13}. Traditional ways that are employed for water treatment are illustrated in figure 1\textsuperscript{14}.

![Figure 1: Traditional ways for water treatment](image)

Since the water treatment process is quite complex, the focus will only be given to the disinfection stages which are the most critical steps. To ensure proper disinfection, organic matter and other materials must be removed prior to disinfection. The vital feature about disinfection is that it leaves a residue to prevent re-growth of microorganisms. This residue is crucial to maintain the purity of the water as it is being delivered to the consumer. The main disinfectant that is being use worldwide is chlorine since its cheap, relatively effective method of killing most waterborne microorganisms, and protecting water from further growth of microorganisms as it travels through a delivery system\textsuperscript{15}.

Despite this, chlorine has several drawbacks such as combining with organic matter in the water to form dangerous organo-chloride by-products such as trihalomethanes (THM) and haloacetic
acids (HAAs). These compounds have been known to cause bladder or rectal cancer. Chlorine is also responsible for the production of other organo-chlorides which are toxic and hazardous to humans. Other disinfectants also being used are sodium/calcium hypochlorite and chloramines. The advantages of using sodium hypochlorite is that it gives the same efficacy and residue protection as chlorine gas but requires less regulation and training than when chlorine is used. Despite this, these alternatives to chlorine also have several limitations. For example, they have a limited shelf life, they produce similar by-products as chlorine gas, they are expensive and require special handling due to their corrosive nature. Chloroamination involves mixing chlorine and ammonia in water to create chloroamines. These can also disinfect the water without formation of trihalomethanes. However, chloroamination lacks the disinfectant strength of chlorine, the water being treated usually requires a second dose of the chemical.

Another traditional treatment method involves the use of adsorption by granular or powdered activated carbon. Activated carbon is an effective adsorbent that is typically used to remove contaminants from water. Granular activated carbon is used in a fixed-bed process like granular media filtration whereas powdered activated carbon (PAC) is added to water as a suspension, allowed to adsorb constituents from water, and is then separated from the finished water. GAC is most commonly incorporated in water treatment facilities for removal of trace contaminants and removal of dissolved organic carbon (DOC). GAC consist of charcoal that has extensive porosity characteristics (between 100 to 500 square meters of surface area per gram of material) for adsorption of contaminants.

1.2.4.1 Mechanism for microconstituent removal by adsorption

Activated carbon operates through adsorption which refers to a process where the compounds in the liquid phase accumulate on a solid surface. The process involves the adsorbate, the dissolved compound that undergoes adsorption, being transported via diffusion into the porous absorbent, the solid onto which the adsorbate adsorbs to. The solute is attached to the absorbent surface through either chemical bonds (chemisorption) or physical attraction (physical adsorption). Physical adsorption is a rapid process caused by non-specific binding mechanisms. It is a reversible process in which the contaminants can be desorbed back into the solution if the concentration of contaminants decreases. Chemisorption on the other hand is a more specific interaction because the adsorbate shares electron density with the adsorbent, forming a higher energy bond.
Adsorption of microconstituents to activated carbon depends on the properties of water, activated carbon, and the microconstituents\textsuperscript{17}. More nonpolar, more hydrophobic and lower solubility compounds should be removed efficiently by carbon adsorption. For activated carbon, lower MW compounds are more efficiently removed because of increased accessibility to inner pores of the carbon, which is the opposite of reverse osmosis. In addition, uncharged molecules are more efficiently removed because of the increased aqueous solubility of charged compounds. Activated carbon has a nonpolar surface at a neutral pH\textsuperscript{17}. Because water is a polar liquid, nonpolar organics are hydrophobic and have lower aqueous solubility. Thus neutral hydrophobic compounds have the strongest affinity to carbon surface.

Adsorption of contaminants onto activated carbon does not degrade or destroy them, they are just transferred to the activated carbon surface. In practice the carbon is usually discarded when it reaches capacity, and so care must be taken that the adsorbed contaminants (e.g. pharmaceuticals and personal care products (PPCPs)) are not slowly released to the environment from the surface of the carbon.

1.2.4.2 Powdered activated carbon vs granular activated carbon

The main difference between these two materials is the size of the activated carbon particles. GAC is typically 0.5 to 3.0 mm in diameter and is used in a fixed-bed process like a granular media filter, whereas PAC is 20 to 50 µm in diameter and added to water in powder form. The principles, advantages and disadvantages are shown in table 1 below\textsuperscript{17}:
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Granular activated Carbon (GAC)</th>
<th>Powder Activated Carbon (PAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal uses</td>
<td>-Control of toxic organic compounds present in groundwater.</td>
<td>Seasonal control of taste and odour compounds and strongly adsorbed pesticides and herbicides at low concentration (&lt; 10 µg/L)</td>
</tr>
<tr>
<td></td>
<td>- Barriers to occasional spikes of toxic organics in surface waters and control of taste and odour compounds.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-Control of disinfection by-product precursors or DOC</td>
<td></td>
</tr>
<tr>
<td>Advantageous</td>
<td>-Can be regenerated (after heat treatment)</td>
<td>Easily added to existing coagulation facilities for occasional control of organics.</td>
</tr>
<tr>
<td></td>
<td>-Lower carbon usage rate per volume of water treated compared to PAC.</td>
<td></td>
</tr>
<tr>
<td>Disadvantageous</td>
<td>-Need contactors and yard piping to distribute flow and replace exhausted carbon.</td>
<td>-Impractical to recover from sludge coagulation facilities.</td>
</tr>
<tr>
<td></td>
<td>-Previously adsorbed compounds can desorb and in some cases appear in the effluent at concentrations higher than present in influent</td>
<td>- Much higher carbon usage rate per volume of water treated as compared to GAC.</td>
</tr>
</tbody>
</table>

Table 1: Principles, advantages and disadvantages of GAC and PAC

1.2.5 Advanced oxidation processes for water purification.

In general, the destruction of hazardous organic waste from various applications including industry, military and commercial process presents greater challenges. Advanced Oxidation Processes (AOPs) have been developed in an attempt to overcome this problem, and have been investigated for the destruction of these classes of compounds when they are present either in
very high concentrations or are very dilute contaminants in aqueous solution. Conventional
destruction of these materials when they are present in high concentrations has involved
methods such as incineration. However, this creates serious problems like releasing toxic
compounds such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated
dibenzo-furans (PCDFs) into the environment via the incinerator off gas emissions and/or fly
ash. AOPs can be broadly defined as aqueous phase oxidation methods based on the
intermediary of highly reactive species such as (primarily but not exclusively) hydroxyl
radicals in the mechanisms leading to the destruction of the target pollutant. Different AOPs
involve different reaction routes yet possess the same basic features with respect to the
production of hydroxyl radicals (OH). These hydroxyl radicals (OH) are extraordinary
reactive species which attack most organic molecules with rate constants usually in the order
of $10^6$-$10^9$ M$^{-1}$s$^{-1}$. Examples of different Advanced Oxidation Processes (AOPs) are listed
in table 2.

<table>
<thead>
<tr>
<th>Method</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}_2/\text{Fe}^{2+}$</td>
<td>Fenton</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2/\text{Fe}^{3+}$</td>
<td>Fenton-like</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2/\text{Fe}^{3+}$ (Fe$^{3+}$/ UV)</td>
<td>Photo assisted Fenton/ UV</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2/\text{Fe}^{4+}$-Oxalate/ UV</td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$/ Oxalic acid/ Ozone/ UV</td>
<td></td>
</tr>
<tr>
<td>$\text{TiO}_2$hv/O$_2$</td>
<td>Photocatalysis</td>
</tr>
<tr>
<td>O$_3$/H$_2$O$_2$</td>
<td></td>
</tr>
<tr>
<td>O$_3$/H$_2$O$_2$</td>
<td></td>
</tr>
<tr>
<td>O$_3$/UV</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$/UV</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Different Advanced Oxidation Processes

There are a variety of processes used to generate hydroxyl radicals. Firstly, Fenton processes
involve the production of hydroxyl radicals using Fenton’s reagent in conjunction with
hydrogen peroxide. This is a vital process involving hydrogen peroxide and will be discussed
further in this chapter under the hydrogen peroxide section. Photo-assisted Fenton processes also exist, which involve the acceleration of hydroxyl radical production through irradiation with UV/visible light. The UV-ferrioxalate system is a further improvement on the Fenton reaction. Ferrioxalate can be irradiated with UV light in an acidic solution to produce carbon dioxide and ferrous ions. This, in combination with hydrogen peroxide, provides a continuous supply of the Fenton’s reagent.

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Photocatalytic processes can also be a medium for hydroxyl radical production. These processes use a semiconductor metal oxide as a catalyst and oxygen as the oxidizing agent. The anatase form of TiO₂ seems to be the most appropriate catalyst tested so far. The ozone/water system utilizes the short lifetime of ozone in aqueous solution. Ozone decomposition proceeds via the formation of hydroxyl radicals. It is possible to enhance this decomposition by adding hydrogen peroxide to the system. The Mn²⁺/oxalic acid system also intensifies ozone decomposition. Hydrogen peroxide photolysis involves irradiating pollutant solutions that contain hydrogen peroxide with UV radiation. The wavelength of light used is less than 280 nm. This causes the homolytic cleavage of the hydrogen peroxide which results in hydroxyl radicals. The final advanced oxidation system is the ozone/UV system. Here, aqueous solutions are saturated with ozone and then irradiated with UV radiation of 254 nm. This is a very complex system due to the large variety of possible reaction pathways.

All of these processes involve the production of hydroxyl radicals. However, hydroxyl radicals are very non-specific in their reactivity, so the activation of hydrogen peroxide to give hydroxyl radicals was not the target outcome of the metal catalysts investigated in this study.

1.2.5.1 Treatment with Ozone and Advanced Oxidation Treatment.

Due to the problems caused by using chlorine, treatment nowadays has shifted focus to more benign and safer methods involving ozone and other AOP (advanced oxidation processes).

Ozone

Another widely used disinfectant apart from chlorine is ozone (O₃). Ozone has been used since it has the ability to disinfect water 100 times faster than chlorine and has been claimed to leave very few residual by-products. Ozone is a very effective oxidant that will react with double bonds, activated aromatic compounds, and deprotonated amines. Ozone works well in destroying selected pharmaceuticals due to formation of hydrogen peroxy anions (HO₂⁻) and
hydroxyl radicals (·OH) that work as powerful oxidizing agents and play an active role in the disinfection process. Production of active radical species is shown in Equation 1\textsuperscript{15}.

\[
\begin{align*}
\text{O}_3 + \text{OH}^- & \rightarrow \text{HO}_2^- + \text{O}_2 \\
\text{O}_3 + \text{HO}_2^- & \rightarrow \cdot\text{OH} + \text{O}_2^- + \text{O}_2
\end{align*}
\]

Equation 1: Production of active radical species

Ozone reacts with organic compounds through a direct pathway by molecular ozone and a radical pathway by means of hydroxyl radicals. Under acidic conditions and in presence of radical scavengers which inhibit the chain reaction which accelerates the decomposition of O\textsubscript{3}, the direct ozonation pathway dominates but under basic conditions or in presence of solutes which promote the radical-type chain reaction which accelerates the transformation of ozone into •OH radicals the latter, i.e. hydroxyl radical reactions dominate\textsuperscript{24,25}. When the medium is basic, O\textsubscript{3} decomposes to generate hydroxyl radicals, which are non-selective and highly reactive oxidants for destruction of toxic organic compounds in wastewater\textsuperscript{24}.

Examples of pharmaceuticals that can be completely degraded using ozone include carbamazepine, diclofenac, EE\textsubscript{2}, BPA, TCS, sulfamethoxazole and roxithromycin\textsuperscript{17,26}. Advantages of ozone over chlorine include the production of no harmful residual by-products and no re-growth of microorganisms. It can be generated on-site hence minimizing problems associated with shipping and handling. Its efficiency not affected by pH in the range (pH 5-8) and it can provide a better taste to the water and better odour control than chlorination. Nevertheless, the downside of using ozone is that it’s more expensive since longer contact times or higher doses are required than are used for disinfection\textsuperscript{27}. In addition, ozone is believed to form harmful by-products (bromate ions, brominated organics and ketones)\textsuperscript{13} and is more complex to handle than the chlorine system as it requires corrosion-resistant materials due to ozone being reactive, toxic and corrosive.
UV light treatment

This technique was first used backed in the US in 1916 and has been proven to be a promising method to treat small municipal water systems. UV light is formed by striking an electric arc through low-pressure mercury vapour which creates two intense peaks at wavelengths 253.7 nm and a lesser peak at 184.9 nm. This UV light is powerful enough to produce ozone, hydroxyl and other free radicals that destroy bacteria\textsuperscript{13}. The advantages using this techniques is that it has no danger of overdose, no known toxic or significant nontoxic by-products, is effective against destroying Cryptosporidium and naturally exhibits no chemical generation, storage, or handling problems. However, the usage of this technique is being restricted due to its expensive cost compared to chlorine, no taste and odour control, less effectiveness in turbid water and no residue protection for drinking water\textsuperscript{13}. Studies also show the combination of UV light and peroxide is a more effective approach in degrading many pollutants\textsuperscript{17,27}. This most probably occurs due to enhanced production of free radical compounds. The advantages of this combination is that hydrogen peroxide is quite stable and can be stored on site for long periods prior to use but unfortunately these system still expensive and require special reactors designed for UV illumination. On top of that hydrogen peroxide has poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, then most of the light input to the reactor will be wasted\textsuperscript{17}.

\subsection*{1.2.5.2 Advantages and disadvantages of (AOPs) in general}

\textbf{Advantages}

Overall AOPs hold greater distinct advantages over traditional treatment processes because they are very effective at removing resistant organic compounds, are capable of completely mineralizing organic contaminants into carbon dioxide if desired, they are less susceptible to the presence of toxic chemicals and they produce less harmful by-products than, for example chlorination. Even though hydroxyl radicals are very unstable in water, the use of AOPs can lower the effective concentration of oxidants required for disinfectant. Hence AOPs should offer some benefits for microbial control\textsuperscript{22}.

\textbf{Disadvantages}

Applications involving ozone are expensive hence their applications should be used cautiously\textsuperscript{22}. Moreover, another growing concern related to ozone applications are that bromide
ions in water can be oxidized into bromate ions and other harmful bromine-containing organic-by-products28,29.

The other limitation using AOPs is that this method is only applicable for wastes with relatively small COD contents (≤ 5.0 g/l) since waste with higher COD content would require the consumption of large amounts of expensive reactants22. Significant disadvantages with respect to Fenton chemistry are that the application requires strict pH control and sludges can be formed with related disposal problems22. In addition, photocatalysis also have several drawbacks especially due to significant recombination of electron-hole pairs hence reducing quantum yield.

This method is still in the R&D stage thus not practical on an industrial scale. Other limitations also include inhibition due to the presence of scavengers, processes that waste light input, mass transfer limitations and the need for additional equipment, construction materials and evaluation costs22.

1.2.6 General EDC and Pharmaceuticals

The existence of active pharmaceutical ingredients and endocrine disrupting contaminants (EDCs) in drinking water has become the major concern for the last three decades. Nevertheless, this issue has already been raised in society for the past sixty years but did not receive significant attention due to lack of sophisticated analytical instruments such as liquid chromatography and mass spectrometry which are able to detect these contaminants in small (i.e. ng/L or parts-per-trillion) concentrations in which steroid hormones, or more broadly all pharmaceuticals and EDCs persist in the environment30. Several studies have been done in US to measure the quality of drinking water31,32 and the most recent ones have discovered33,34 that roughly 36 pharmaceuticals and EDCs are found in the water before and after treatment at one particular US drinking water treatment plant (DWTP). The list of chemicals present is presented in table 3 below showing the different concentrations33,34.
<table>
<thead>
<tr>
<th>Class</th>
<th>Method</th>
<th>MRL (ng/L)</th>
<th>MW</th>
<th>( pK_a )</th>
<th>( \log K_{ow} )</th>
<th>S (mg/L)</th>
</tr>
</thead>
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<tr>
<td>Acetaminophen</td>
<td>Pharmaceutical</td>
<td>LC</td>
<td>1</td>
<td>151.2</td>
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<td>286.4</td>
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<td>Pesticide</td>
<td>LC</td>
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<td>215.7</td>
<td>1.7</td>
<td>2.61</td>
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<tr>
<td>Benzo[a]pyrene</td>
<td>PAH</td>
<td>GC</td>
<td>10</td>
<td>252.3</td>
<td>NA</td>
<td>6.13</td>
</tr>
<tr>
<td>Caffeine</td>
<td>PCP</td>
<td>LC</td>
<td>10</td>
<td>104.1</td>
<td>10.4</td>
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<td>236.3</td>
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<td>GC</td>
<td>10</td>
<td>354.5</td>
<td>NA</td>
<td>6.91</td>
</tr>
<tr>
<td>DEET</td>
<td>PCP</td>
<td>LC</td>
<td>1</td>
<td>191.3</td>
<td>0.67</td>
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<td>Pharmaceutical</td>
<td>LC</td>
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<td>284.7</td>
<td>3.4</td>
<td>2.82</td>
</tr>
<tr>
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<td>Pharmaceutical</td>
<td>LC</td>
<td>1</td>
<td>294</td>
<td>4.51</td>
<td>0.7</td>
</tr>
<tr>
<td>Dilantin</td>
<td>Pharmaceutical</td>
<td>LC</td>
<td>1</td>
<td>252.3</td>
<td>8.33</td>
<td>2.47</td>
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<tr>
<td>Erythromycin-H2O</td>
<td>Antimicrobial</td>
<td>LC</td>
<td>1</td>
<td>734.5</td>
<td>8.88</td>
<td>3.06</td>
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<td>Estradiol</td>
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<td>LC</td>
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<td>272.4</td>
<td>10.4</td>
<td>4.01</td>
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<td>Estrone</td>
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<td>270.4</td>
<td>10.4</td>
<td>3.13</td>
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<td>Ethynylestradiol</td>
<td>Steroid</td>
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<td>296.4</td>
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<td>3.67</td>
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<td>Fluorene</td>
<td>PAH</td>
<td>GC</td>
<td>10</td>
<td>166.2</td>
<td>NA</td>
<td>4.18</td>
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<tr>
<td>Fluoxetine</td>
<td>Pharmaceutical</td>
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<td>309.1</td>
<td>8.7</td>
<td>4.05</td>
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<td>Galaxolide</td>
<td>Fragrance</td>
<td>GC</td>
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<td>258.4</td>
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<td>Gemfibrozil</td>
<td>Pharmaceutical</td>
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<td>250.3</td>
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<td>299.4</td>
<td>7.32</td>
<td>2.16</td>
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<td>Ibuprofen</td>
<td>Pharmaceutical</td>
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<td>206.3</td>
<td>4.91</td>
<td>3.97</td>
</tr>
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<td>Iopromide</td>
<td>Pharmaceutical</td>
<td>LC</td>
<td>1</td>
<td>791.1</td>
<td>10.2</td>
<td>-2.05</td>
</tr>
<tr>
<td>Lindane</td>
<td>Pesticide</td>
<td>GC</td>
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<td>290.8</td>
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<td>Meprobamate</td>
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<td>218.3</td>
<td>10.9</td>
<td>0.7</td>
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<tr>
<td>Metolachlor</td>
<td>Pesticide</td>
<td>GC</td>
<td>10</td>
<td>283.8</td>
<td>-1.34</td>
<td>3.13</td>
</tr>
<tr>
<td>Musk Ketone</td>
<td>Fragrance</td>
<td>GC</td>
<td>10</td>
<td>204.3</td>
<td>NA</td>
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<tr>
<td>Naproxen</td>
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<td>230.3</td>
<td>4.15</td>
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<td>Oxybenzone</td>
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<td>LC</td>
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<td>228.1</td>
<td>7.77</td>
<td>3.79</td>
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<td>Pentoxifylline</td>
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<td>1</td>
<td>278.3</td>
<td>0.97</td>
<td>0.29</td>
</tr>
<tr>
<td>Progesterone</td>
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<td>314.5</td>
<td>NA</td>
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<td>Sulfamethoxazole</td>
<td>Antimicrobial</td>
<td>LC</td>
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<td>253.3</td>
<td>5.5</td>
<td>0.89</td>
</tr>
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<td>TCEP</td>
<td>PCP</td>
<td>LC</td>
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<td>287.5</td>
<td>7.9</td>
<td>4.76</td>
</tr>
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<td>Trimethoprim</td>
<td>Antimicrobial</td>
<td>LC</td>
<td>1</td>
<td>290.3</td>
<td>7.12</td>
<td>0.91</td>
</tr>
</tbody>
</table>

NA = Not applicable; MRL = Method reporting limit.

Table 3: Contaminants in wastewater
This evidence was further supported by research done by Benotti in 2009 that discovered the existence of 51 pharmaceutical and EDCs in 19 sources of water, in 18 sources of purified and treated water and 15 distributed system waters from utilities in US\textsuperscript{35}.

These early studies have indicated how critical the situation is whereby these chemicals are found in drinking water nowadays. This major concern requires an immediate response to be taken to overcome this problem. Recent studies show huge evidence of decrease population of fish and amphibians due to the exposure to EDCs. For example marine gastropods exposed to tributyltin compounds, which leach from certain antifouling paints and PVC pipes, experienced severe decreases in the population and reproductive disorders including imposex\textsuperscript{36}. In certain cases, especially in amphibian populations, supernumerary limbs and missing limbs have been attributed to certain pesticides and other anthropogenic chemicals\textsuperscript{37}. Another study in the US also shows that fish that inhabit the area below a wastewater treatment plant show severe reproductive abnormalities including changes in the levels of sex steroids, gonadal histology (e.g. hemaphrodism and intersex), and increased levels of the female egg yolk precursor, vitellogenin, in male fish. Collectively, these impacts of wastewater effluent on male fish are referred to as feminization because fish that are genetically male exhibit female sex characteristics\textsuperscript{38}. Some examples of estrogenic compounds are shown in Figures 2-7\textsuperscript{39}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{DDT on left and Octyphenol on the right}
\end{figure}
Figure 3: Bisphenol A on the left and Methoxychlor on the right

Figure 4: 17-α Ethynylestradiol on the left and 17β-Estradiol on the right

Figure 5: Bezafibrate on the left and Clofibrac acid on the right
Figure 6: Carbamazepine on the left and Diclofenac on the right

Figure 7: Primidone

The existing methods used to remove these pharmaceutical and EDCs mainly depend on the structure and concentration of the contaminant itself. For example chemical oxidation (during drinking water applications), biological removal/transformation (during wastewater applications), or nanofiltration/reverse osmosis membrane technologies have all been used. In addition, parameters such as oxidant dose and contact time also determine the degree of attenuation of a particular contaminant\textsuperscript{40}.

1.2.6.1 Method to remove EDCs and pharmaceuticals from drinking water

Recent studies indicate that membrane application such as ultra-filtration (UF), reverse osmosis (RO), nano-filtration (NF) and micro-filtration (MF) are among the membranes that show potential in removing organic contaminants from water. RO is normally used for either desalination or RO pre-treatment processes. MF and UF are normally recommended when there are space limitations and/or variable feed water quality\textsuperscript{41}.
1.2.6.1.1 UV-light based applications; UV/H$_2$O$_2$ and VUV

This method is normally used for disinfection and the mechanism generally involves the interaction of artificial or natural light with the target molecules and compounds which then lead to a series of photochemical reactions$^{42}$. Features such as the ability of the compounds to absorb light, play an important role in direct photolysis processes. The efficiency of direct photolysis is enhanced when irradiation is combined with hydrogen peroxide, whose photocatalytic dissociation yields (-OH)$^{43}$ which later on assist degradation and disinfection. H$_2$O$_2$/UV and VUV (visible ultraviolet) is eight times more effective compared to direct UV-photolysis$^{42}$.

Nevertheless, this method is only successful in significantly lowering the natural organic matter (NOM) if high levels of peroxide and UV light are used. However the use of excess amounts of hydrogen peroxide is not preferable since it can cause the formation of (-OH) scavengers thus the optimum H$_2$O$_2$ concentration should be around 0.0032 M to 0.0163 M.

The drawback in using this method, particularly in VUV, is the formation of undesired-by-products such as nitrite. Despite this, the formation of nitrite can be avoided by using UV/VUV with the addition of ozone$^{44}$.

1.2.6.1.2 Ozone based applications: O$_3$/H$_2$O$_2$, O$_3$/UV, O$_3$/H$_2$O$_2$/UV and O$_3$/H$_2$O$_2$/TiO$_2$

Ozone has long been known for its useful purposes including odour management, disinfection and taste. Ozone works by reacting with NOM by an electrophilic addition to a double bond which is very selective. In addition to the direct reaction of ozone with NOM, non-selective and fast reactions occur with (-OH) that are formed when the reduction potentials for ozone and (-OH) are +2.42 and -2.86 eV, respectively (referenced to standard hydrogen electrode)$^{45}$. Even though the ozonation process itself can be describe as an advanced organic product (AOP), so far only a combination of processes have been investigated. Ozone-AOP systems have been studied recently as disinfection and detoxification methods of pollutants in different types of water$^{46}$. Further studies reveal that NOM can be removed using an ozone-AOP technique where adding H$_2$O$_2$ to the ozonation process can improve the reduction of DOC (dissolved organic carbon) compared to ozone alone$^{47}$. Few studies exist where ozone- AOP is used in NOM removal. Adding the H$_2$O$_2$ into the ozonation process has been concluded to enhance the reduction of DOC compared to the ozone alone$^{47}$. In addition it was also discovered that the post-ozonation O$_3$/H$_2$O$_2$ system achieves better removal of DOC compared to the pre-ozonation O$_3$/H$_2$O$_2$-system. However, trihalomethane (THM) concentrations were higher in
both the post- and pre-treated O$_3$/H$_2$O$_2$ samples compared to ozonated samples$^{47}$. Overall, O$_3$/UV is the most significant combination of parameters that are effective in the mineralization of DOC$^{45}$.

1.2.6.1.3 Catalytic Oxidation
Aqueous H$_2$O$_2$ decomposes over heterogenous catalysts such as metals (e.g. Fe, Cu, Pt, Ti and Ni) and metal oxides immobilized on various support materials (such as sand, silica, zeolites and alumina)$^{48}$. With respect to Fenton chemistry, peroxide decomposition occurs through the surface of catalysts which lead to the formation of strong oxidants including OH radicals$^{49}$. Early studies shows several oxidants have also been investigated such as sulfate radical-based AOPs involving the use of peroxymonosulfate and persulfate as precursor oxidants$^{50}$. Overall, it was discovered that chelating agents are able to improve the efficiency of Fenton-like reactions$^{51}$. Research also shows that catalytic ozonation can double the efficiency of NOM removal from water when compared to ozonation alone, and catalytic ozonation with MnO$_2$ has been observed to improve the elimination of NOM measured as total organic content (TOC) and carbon oxygen demand (COD)$^{52}$.

1.2.6.1.4 Fenton Processes
The usual process around Fenton chemistry involves the use of hydrogen peroxide as the initial oxidizing agent and an iron (II) catalyst either as metal salt or metal oxide. There are three main types of Fenton reaction. These are the thermal or classical Fenton reaction, the photo-Fenton reaction, and finally the electro-Fenton reaction$^{53}$. Photo-Fenton reaction in particular proceeds by irradiation with sunlight or an artificial light source, which leads to the formation of ·OH, hence increasing the rate of organic compound or contaminant degradation$^{54}$. Studies on Fenton chemistry have shown that the UV/Fe (III)/H$_2$O$_2$ system can remove significant amount of organic compounds with lower molar masses across a wide range of pH values between 3 to 7 which makes it potentially feasible and cost-effective for large scale application.

Despite the fact that removal of large amounts of NOM has been detected, the organic compounds that remain in the water have been observed to be fairly reactive to chlorine, thus leading to minimal reduction of trihalomethane formation potential (THMFP)$^{55}$. Another aspect about photo-Fenton processes is the use of UV or solar light as a source of irradiation for degradation and mineralisation of phenol which is good in terms of economic and environmental perspectives$^{56}$.
1.2.6.1.5 Miscellaneous treatment

1.2.6.1.5.1 Removed Endocrine disruptor compound (EDC) using surface modified NF membranes

Various potential physical treatment methods have been investigated. However, only nanofiltration (NF) has been fully explored because of its numerous advantages, including relatively high removal efficiency of organic micro-pollutants, no formation of toxic reaction by-products and ease of operation\(^57\). Since the removal efficiency of the NF membrane depends on the interaction between the membrane and the target compounds, it has been shown that modifying existing NF membranes using free-radical graft polymerization techniques before further cross-linking and modification via functional group substitution could improve rejection of EDCs.

This modification was done using thin film composite (TFC) polyamide (PA) nanofiltration (NF) membranes with methacrylic acid (MA) as the monomer for graft polymerization. MA reacts in DI water with sodium metabisulfite and \((\text{Na}_2\text{S}_2\text{O}_5)\) and sodium persulfate \((\text{Na}_2\text{S}_2\text{O}_8)\) which provide \((·\text{OH})\) for growth of polymer chain. This was followed by reaction with succinic acid (SA) and ethylene diamine (ED) where both act as functional group modifiers. In this reaction, ED also acts as a cross-linker. This MA membrane can further undergo modification with water-soluble carbodiimide (WSC) and N-hydroxysuccinimide (NHS) (figure 8). WSC assists the formation of amide bonds between the primary amines in ED and the carboxylic acid on the MA membrane while NHS enhances reaction yield. Overall, this graft polymerization of MA on the raw NF membrane increased the hydrophilicity and negative surface charge of the membrane in proportion to the amount of carboxylic acid in the grafted polymer chains. Increasing the steric hindrance and negative surface charge of the MA-membrane improved rejection of the target pollutants; BPA and EDCs. However, excessive polymerization times negatively affected water permeability\(^57\). By further cross-linking the MA-membrane with ED, rejection of uncharged BPA was improved relative to that of the MA-membrane but decreased for negatively charged solutes due to loss of negative surface charge on the MA-membrane upon cross-linking. Unfortunately, the water flux with the cross-linked membrane decreased severely due to the increased hydraulic resistance compared to the MA-membrane.
Figure 8: Schematic of membrane modification: (a) graft polymerization and (b) cross-linking of grafted polymer chains and substituting functional groups
1.2.6.1.5.2 Combination of nanofiltration membrane and homogeneous catalytic oxidation to remove endocrine disrupting chemicals (EDCs)

A more recent study also showed promising ways to destroy EDCs using a novel hybrid system that combines the advantage of having homogenous catalytic oxidation and nanofiltration for the effective removal of BPA. This is because even though NF can provide high removal rate of low molecular weight organic micropollutants\textsuperscript{58,59}, NF itself does not destroy micropollutants and hence requires the disposal of concentrated pollutants. In addition extra cost for mineralization is needed to treat pollutants accumulated in the NF retentate. Homogenous catalytic oxidation using iron (III)-tetrasulfophthalocyanine (Fe(III)-TsPc) and hydrogen peroxide as an oxidant was studied\textsuperscript{60}. The reaction rate of this catalyst is faster in homogeneous systems rather than in heterogeneous systems. Despite that, the drawback of using this system is the ease of separation between the catalyst and the feed stream. A schematic diagram of how the system works shown below (figure 9):

![Schematic diagram of nanofiltration system](image)

**Figure 9**: Schematic diagram of nanofiltration system

using a combination of Fe(III) TsPC/H\textsubscript{2}O\textsubscript{2} and NF membrane enhanced removal of BPA was compared with a conventional NF system itself. In the NF hybrid system, BPA removal
efficiency was >95% throughout the entire duration of operation due to continuous decomposition of BPA in the retentate by catalytic oxidation. In addition, only the monomeric form of Fe(III)-TsPc appears to be the most effective form for the decomposition of BPA. This catalytic oxidation is dependent on hydrogen peroxide concentration and pH. Hence if the reaction is not taken to completion, intermediates and by-product are formed, for example p-benzoquinone, hydroquinone, 1-methyl-4-(prop-1-en-2-yl)benzene, and 4-(2-(4-hydroxyphenyl)propan-2-yl)cyclohexa-3,5-diene-1,2-dione. The structure of these intermediate are shown below in Figure 10:

Figure 10: Intermediates and by-products from the reaction of Fe(III)\textsuperscript{3+}TsPC/H\textsubscript{2}O\textsubscript{2} and a NF membrane

Stable retention of Mg\textsuperscript{2+} during 70 h of operation suggests that catalytic oxidation did not damage the NF membrane. Nevertheless, the water permeability and rejection capacity of the NF membrane were affected by aggregation of the catalyst on the membrane surface.
1.2.6.1.5.3 Removal of EDCs such as TCS using the enzyme laccase immobilized on mesoporous nanofibres

5-Chloro-2-[2,4-dichlorophenoxy]-phenol), which is known as Triclosan is an antimicrobial agent widely used in a range of pharmaceuticals, personal and health care products. As a result, TCS has been listed as the 7th most frequently detected compound in water in the US with the median concentration of 140 ng/L. Thus growing concern regarding existence of TCS in aquatic environments has become a major issue since various studies show that TCS not only can be converted to 2,8-dichlorodibenzo-p-dioxin which is carcinogenic but also can have a negative effect on a range of aquatic organisms.

Since most of the methods currently used now suffer from several limitations, for instance chlorination treatment produces various intermediates or by-products that are more toxic than the parent compounds, researchers have tried to find alternative routes to treat water that are more economical, environmental friendly and efficient.

One possible method of treatment involved the use of the enzyme laccase which has a high adsorption capacity on mesoporous materials. Laccase enzyme was used since it is known to be a highly selective catalyst that accelerates both the rate and specificity of pollutant degradation under mild conditions. Despite that, homogenous reactions involving laccase are limited by low stability, short lifetime and high price. Mesoporous nanofibrous membranes have been typically used for enzyme immobilization since they can increase enzyme loadings (large surface area) and enhance enzyme performance.

By immobilizing laccase on electrons spun microporous nanofibrous membranes, superior systems have been developed where the immobilized enzyme can be recycled and reused during water treatment. On top of that, enzyme immobilization and stabilization could efficiently prevent the leaching of enzyme in larger mesoporous pores and improve properties of materials that are used repeatedly.

This system can achieve loadings of laccase as high as 420 mg/g while the catalytic activity of the laccase is still highly retained. About 65% TCS was removed at pH 4, at a temperature of 30°C in 2 hours reaction. Overall schematic reaction is shown in Figure 11 below:

25
1.3 Hydrogen peroxide chemistry

1.3.1 Hydrogen peroxide as an Oxidant

Hydrogen peroxide is a popular oxidizing agent that is used in considerable amounts for bleaching in the pulp and paper industry. In order to ensure optimum use and selectivity of hydrogen peroxide, an appropriate catalyst can be used to assist this bleaching reaction. Despite hydrogen peroxide being known as a strong oxidant, its reaction rate, with organic compounds, is often slow at ambient conditions and it has low selectivity\textsuperscript{69}.

Moreover, H\textsubscript{2}O\textsubscript{2} has also been reported to have low toxicity towards humans and it only becomes significantly hazardous when the concentration is greater than 10\% with continuous ingestion. One of the most important potential hazards when handling H\textsubscript{2}O\textsubscript{2} is that a build-up of pressure can occur if the containment system becomes sealed. This could eventually cause a pressure explosion. The application of heat for the introduction of containments can increase the release of oxygen and the rate of pressure increase in a sealed system.

Another hazard to be aware of is when hydrogen peroxide is distilled under reduced pressure. This concentrates the hydrogen peroxide and at very high concentrations hydrogen peroxide

\textbf{Figure 11: Triclosan removal by laccase immobilized on mesoporous nanofibers: Strong adsorption and efficient degradation}\textsuperscript{68}
can spontaneously explode if it comes into contact with metals, for instance copper, iron, manganese, nickel, or chromium or organic compounds, such as ethers and acetics. Upon being heated, hydrogen peroxide will also decompose into water and oxygen.

Hydrogen peroxide is usually manufactured commercially by the autoxidation of 2-ethyl-9, 10-dihydroxyanthracene producing 2-ethylanthraquinone and hydrogen peroxide using oxygen from the air (see Figure 12). The anthraquinone derivative is extracted out and reduced back to the dihydroxy compound using hydrogen gas in the presence of a metal catalyst. Approximately 2.2 million metric tonnes of hydrogen peroxide is produced annually worldwide with approximately 50% being used for pulp bleaching and 10% for textile bleaching.

Figure 12: Commercial preparation of hydrogen peroxide from auto-oxidation of 2-ethyl-9, 10-dihydroxyanthracene

Hydrogen peroxide is a weak acid (pKa = 11.65 at 25°C) that is related to its conjugated base through the pH dependent equilibrium (shown in Equation 2)

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOO}^- + \text{H}_3\text{O}^+
\]

Equation 2: pH dependent equilibrium of hydrogen peroxide

The decomposition of hydrogen peroxide to oxygen and water is catalysed by a number of metal ions and metal compounds. Although bases can catalyse this decomposition, aqueous transition metal catalysed decomposition is approximately 1,000 times faster at pH 11.6. The base catalysed decomposition is shown in the Equation 3 below:
Equation 3: Base catalysed decomposition of hydrogen peroxide

\[
\begin{align*}
H_2O_2 + OH^- & \rightarrow HOO^- + H_2O \\
H_2O_2 + HOO^- & \rightarrow O_2^- + HO^- + H_2O \\
H_2O_2 + O_2^- & \rightarrow HO^- + OH^- + O_2 \\
HO^- + HOO^- & \rightarrow O_2^- + H_2O
\end{align*}
\]

Equation 4: Proposed steps in the mechanism for metal catalysed hydrogen peroxide decomposition

The mechanism of the metal ion catalysed decomposition is more complex and is assumed to proceed via the steps depicted in Equation 4. It is the hydroperoxide ion (HOO⁻) that is the focus of non-metal catalysed hydrogen peroxide oxidation. Under basic conditions, the strong HOO⁻ nucleophile is formed which is active for epoxidation of electrophilic alkenes such as unsaturated ketones or carboxylic acid derivatives. However, if the concentration of this ion becomes too high, significant amounts of hydrogen peroxide are consumed by the decomposition reactions outlined in Equation 4. If the concentration of hydroxyl radicals is high, radical oxidation chemistry dominates leading to a reduction in selectivity.
1.3.2 Physical and Chemical properties of Hydrogen Peroxide

Hydrogen peroxide is a clear, colourless liquid which is miscible with water in all proportions. Hydrogen peroxide itself and highly concentrated aqueous solutions (> 65 wt%) are soluble in variety organic solvents such as carboxylic esters\(^73\). Hydrogen peroxide and water do not form an azeotropic mixture and in theory can be separated completely by distillation. In practice, 100 wt% hydrogen peroxide is obtained by fractional crystallization of a highly concentrated (ca. 90 wt %) aqueous solution. Pure 100 wt% hydrogen peroxide is stable at room temperature but is not produced on an industrial scale. Data that show the bonding in H\(_2\)O\(_2\) (obtained by neutron diffraction on solid H\(_2\)O\(_2\)) are shown below in table 4\(^74\):

<table>
<thead>
<tr>
<th>Bond properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length (O-O)</td>
<td>145.3 ± 0.7 pm</td>
</tr>
<tr>
<td>Bond length (O-H)</td>
<td>99.8 ± 0.5 pm</td>
</tr>
<tr>
<td>Bond angle (O-O-H)</td>
<td>102.7 ± 0.3°</td>
</tr>
<tr>
<td>Azimuthal angle</td>
<td>90.2 ± 0.6</td>
</tr>
</tbody>
</table>

Table 4: Bond Properties of H\(_2\)O\(_2\)

As a weak acid, hydrogen peroxide forms salts with various metals. In addition, the redox potential of hydrogen peroxide depends on the pH as shown in the diagram (Figure 13) and in some instances it can itself be oxidised (ie. act as a reducing agent)\(^75\):

![Redox reaction diagram](image)

**Figure 13: Standard potential of redox reaction**

To determine the hydrogen peroxide content of aqueous solutions, potassium permanganate or cerium (IV) sulfate can be used for quantitative determination\(^76\).
Decomposition of hydrogen peroxide occurs by disproportionation (Equation 5)\textsuperscript{73} and is regarded as very important consideration in the handling of hydrogen peroxide, its storage and use in the laboratory.

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2
\]

**Equation 5: Hydrogen Peroxide decomposition**

This reaction is highly exothermic and takes place in the presence of small amounts of catalyst even in aqueous solution. In the absence of a catalyst, it occurs very slowly indeed. Decomposition can be catalyzed both homogeneously by dissolved ions (especially of the metals iron, copper, manganese, and chromium) and heterogeneously by suspended oxides and hydroxides (e.g., those of manganese, iron, copper, palladium, or mercury) and by metals such as platinum, osmium, and silver\textsuperscript{73}.

In addition, hydrogen peroxide can also undergo substitution reactions where the hydrogen atoms of H\textsubscript{2}O\textsubscript{2} can be substituted by alkyl or acyl groups, leading to the formation of compounds shown in Table 5\textsuperscript{73}:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl hydroperoxides</td>
<td>H-O-O-R</td>
</tr>
<tr>
<td>Dialkyl peroxides</td>
<td>R-O-O-R</td>
</tr>
<tr>
<td>Percarboxylic acids</td>
<td>H-O-O-Ac</td>
</tr>
<tr>
<td>Diacyl peroxides</td>
<td>Ac-O-O-Ac</td>
</tr>
</tbody>
</table>

**Table 5: Substitution products of hydrogen peroxide**

### 1.3. 3 Fenton chemistry

Fenton chemistry can be described as the interaction between ferrous salts and hydrogen peroxide to produce a reactive species capable of oxidising a wide variety of organic substrates\textsuperscript{77}. Fenton chemistry was first reported by Henry J. Fenton in the year 1894 when he showed that hydrogen peroxide was activated by Fe(II) salts, resulting in the oxidation of tartaric acid\textsuperscript{78}. This was followed by a report by Haber and Weiss in 1934 which proposed that the active oxidant generated by the Fenton reaction was the hydroxyl radical (HO\textsuperscript{·}), one of the most powerful oxidants known with a reduction potential of $E^0$ values 2.73 V\textsuperscript{78}. These early
studies recognised the importance of the hydroxyl radical as a powerful oxidant for various processes including waste treatment. The Fenton reaction is extremely complex and results in the production of higher oxidation states of iron as well as hydroxyl radicals. There are three main types of the Fenton reaction. These are the thermal or classical Fenton reaction, the photo-Fenton reaction, and finally the electro-Fenton reaction. The classical Fenton reaction, simply stated, involves the decomposition of hydrogen peroxide catalysed by Fe (II) in the absence of light. The process can be shown by a series of seven equations as indicated in Equation 6 below.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \\
\text{HO}^- + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \\
\text{HO}^- + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{Fe}^{3+} + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2\text{H}^+ \\
\text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\end{align*}
\]

**Equation 6: Thermal Fenton and related reactions**

In the absence of other oxidizing substances, the net reaction is catalysed by iron and results in the conversion of \( \text{H}_2\text{O}_2 \) to molecular oxygen and water to a certain extent, this will take place even when a substrate is present. Some of the hydroxyl radicals produced may bind to the iron giving \([\text{Fe}---\text{OH}^-]^{3+}\) or \([\text{Fe}=\text{O}]^{2+}\) intermediates. These intermediates are believed to have similar oxidizing properties to the free hydroxyl radical.

In the photo-assisted Fenton reaction, the reaction solution is irradiated with UV/visible light. This leads to faster reaction rates and higher yields of inorganic degradation products. This enhancement is observed even when the light source is just ordinary fluorescent laboratory lights. This is primarily due to the photochemistry of Fe-(III) species. Fe-(III) complexes are able to undergo a ligand to metal charge transfer excitation, resulting in dissociation to give Fe- (II) (Equation 7):

\[
\text{Fe}^{3+}\text{Ln} + \text{hv} \rightarrow \text{Fe}^{2+}\text{Ln}_n^1 + \text{Ln}^\circ \\
\]

**Equation 7: Ligand to metal charge transfer excitation of Fe (III) complex**
In this reaction, Lₙ represents the ligand set in the Fe-(III) complex. The reduced iron complex can then react with hydrogen peroxide to produce the desired hydroxyl radical\(^{78}\). Furthermore, oxidation of the ligand may result in degradation of the organic substrate. A final advantage to this process is that photolysis of hydrogen peroxide can also occur, which provides more hydroxyl radicals (Equation 8).

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{HO}^-
\]

**Equation 8: Photolysis of hydrogen peroxide**

Lastly, the electro Fenton method is a process where one or more of the reactants is ‘generated in situ’ through electrochemical reactions. The reagents generated depend primarily on the cell potential, the nature of the electrodes and the solution conditions. Possible electron-Fenton reactions are shown below:

![Figure 14: Possible electro-Fenton reactions, reagent produced shown in bold](image)

Even though this ‘in situ’ process can be advantageous, there are still limitations with respect to this method especially the slow production of hydrogen peroxide due to the low solubility of oxygen in water. The hydroxyl radicals produced by the Fenton reaction can undergo a number of reactions with organic compounds. When air is present in the solution, the radicals formed in these reactions can react to give peroxyl or oxyl radicals\(^{78}\). The organic intermediates formed can also react further with hydroxyl radicals leading to eventual mineralization to carbon dioxide, water, and inorganic acids if heteroatoms are present.

A number of issues are associated with the Fenton reaction, for example, the instability of the reagent mixture and the requirement in most cases for acidic conditions. These limit the
widespread use of this process. Also, a large fraction of the bulk oxidant is wasted through conversion to oxygen. Finally, an iron oxide sludge is produced in this process which is difficult to dispose of\textsuperscript{78}.

So far, this description has only considered the reaction between Fe-(II) salts and hydrogen peroxide. In fact, alternative reagents are possible. Fenton himself noted that hypochlorous acid could be used rather than hydrogen peroxide as the oxidant\textsuperscript{80} (Equation 10).

\[
\text{Fe-(II)} + \text{HOCl} \rightarrow \text{Fe-(III)} + \text{HO} \cdot + \text{Cl}^{-}
\]

\textit{Equation 9: Fenton reaction with hypochlorite as the oxidant}

Also, even though the Fenton reagent is typically an iron (II) salt, other metals in low oxidation states are able to be substituted for iron. One such option is copper, however it is difficult to study these reactions, as copper-(I) disproportionate in aqueous solution. Other options include titanium-(III), chromium-(II), cobalt-(II), and vanadium-(II). All these metals are all able to reduce hydrogen peroxide to yield hydroxyl radicals or similar oxidants.

Fenton’s reactions are clearly an important method for the production of hydroxyl radicals from hydrogen peroxide. However, due to the low selectivity of the hydroxyl radicals, the production of iron sludge, and the required acidic conditions, and inefficient use of hydrogen peroxide, this process is far from ideal and is not compatible with many of the principles of green chemistry described earlier in this chapter. In an alternative approach, Professor Collins and his group designed iron- TAML complexes that catalyse oxidations with hydrogen peroxide. The active intermediate in a terminal metal-oxo species. This catalyst will be discussed further in section 1.5.

\subsection*{1.3.4 Biological catalysts for $\text{H}_2\text{O}_2$ oxidation reactions (peroxidases)}

Peroxidases can be defined as heme containing enzymes that utilize hydrogen peroxide to catalyze the oxidation of a wide variety of organic and inorganic substrates.\textsuperscript{81} The general reaction is shown below in Equation 10 (RH\textsubscript{2} represent as general substrate). They have a molecular weight range from 35-000 to 100-000 (from 251-726 residues) and most of the structure contains Heme B except myeloperoxidase\textsuperscript{82}. Native heme peroxidase normally exists as ferriphophorphyrin IX, with four pyrrole-like nitrogen bound to the Fe-(III)\textsuperscript{83}. The fifth coordination position on the proximal side of the heme is usually occupied by the imidazole group of a histidine residue\textsuperscript{83} while the 6\textsuperscript{th} position remains empty. This result in a high spin (S= 5/2) state for the iron\textsuperscript{82}. 

33
Peroxidases can be classified into 3 major groups corresponding to the amino acid sequence homologies. Class I are prokaryotic peroxidases, (e.g. yeast cytochrome c peroxidase and plant ascorbate peroxidases (smallest peroxidase with 251 amino acids)); Class II are secretory fungal peroxidases; and Class III, secretory plant peroxidases (ER-targeted), e.g. horseradish peroxidase isoenzyme C. Class III peroxidases contain structural Ca\(^{2+}\), disulfide bridges and are targeted for the secretory pathway via the endoplasmic reticulum.\(^{83}\)

The main structural point of difference between heme peroxidases and cytochrome P450 is in the way the protein chain binds to the iron centre. In heme peroxidases, the coordination is found through the nitrogen atom of a histidine group whereas the sulfur atom of a cysteine group coordinates to the iron centre in the cytochrome P450.\(^{82}\)

The catalytic process is more complex involving multistep reactions as shown in the reaction below in Equation 11\(^ {81}\).

The catalytic process occurs through a multistep reaction. First, the reaction of the active site of the heme with hydrogen peroxide occurs. This causes the reduction of $H_2O_2$ to water and the oxidation of the protein by two electrons. The latter state of the protein called Compound I, contains a ferryl (Fe-(IV)=O) centre and an organic cation radical which can be located either
on the heme or on a protein residue, depending on the isoenzyme. Then, Compound I oxidizes one substrate molecule (S) to give a substrate radical and Compound II, where the organic cation radical is reduced to its resting state. Finally, Compound II is reduced by a second substrate molecule to the resting iron-(III) state. The exact nature of this mechanism is not known but the overall rate of this mechanism is rapid—(> 10^6 M^-1 s^-1). The exact nature of this mechanism is not known but the overall rate of this mechanism is rapid—(> 10^6 M^-1 s^-1).

1.3.5 Catalase destruction of hydrogen peroxide

Catalase can be defined as a haematin enzyme found in relatively large concentrations in erythrocytes, in the liver, and kidney. It is composed of four identical, tetrahedrally arranged subunits. Each 60 kDa subunit contains a heme group and NADPH in its active centre. Its acts as an extremely efficient catalyst for hydrogen peroxide destruction into water and oxygen as well as ‘peroxidatively’ oxidising alcohols, formate or nitrite ions with hydrogen peroxide. Representative structure of catalase shown below in Figure 15 and Figure 16:

**Figure 16: Structure A**
**Figure 15: Structure B**

**Structure A**: Alpha carbon backbone of one catalase subunit. The heme group is shown with thicker bonds.

**Structure B**: Diagrammatic representation of secondary structural elements.

Despite unknown data to predict specific chemistry regarding catalase catalysis, Jones has proposed that the reaction mechanism would be similar to the mechanism of Cytochrome C peroxidase. The catalytic process for monofunctional catalases follows 2 distinct routes as follows:

35
PorFe$^\text{III}$ + H$_2$O$_2$ $\rightarrow$ Por$^+$Fe$^\text{IV}$=O + H$_2$O \hspace{1cm} (1)

Por$^+$Fe$^\text{IV}$=O + H$_2$O$_2$ $\rightarrow$ PorFe$^\text{III}$ + O$_2$ + H$_2$O \hspace{1cm} (2)

**Equation 12: Propose mechanism of action for Catalase**

The first stages involved the oxidation of the heme iron via hydrogen peroxide to produce compound 1, an iron (IV)-oxoporphyryl radical cation species. This then proceeds with the second stages involving the reduction of compound 1 where the second H$_2$O$_2$ acts as an electron donor providing two oxidation equivalents (compound 2). Instruments such as mass spectrometry and gas chromatography show that in monofunctional catalases, O$_2$ is formed by two-electron oxidation of H$_2$O$_2$ without breaking the O-O bond$^{90,91}$. Reaction 2 was proposed to include proton abstraction by the distal histidine, hydride-ion transfer to Compound I and finally, liberation of dioxygen and water$^{91,92}$.

When hydrogen peroxide enters the active site, it is sterically hindered and interacts with the amino acids His$^{74}$ (histidine at position 74) and Asn$^{147}$ (asparagines at position 147). It is in this position that the first stage of catalysis takes place. In addition, the close proximity of a phenolic side chain from Tyr$^{357}$ (tyrosine at position 357) was believed to enhance the oxidation of Fe$^\text{III}$ to Fe$^\text{IV}$ by acting as the 5$^{th}$heme iron ligand as well as helping in the removal of an electron from the heme ring. Transfer of a proton from the coordinated oxygen of the peroxide to the terminal oxygen, via His$^{74}$, elongates and polarizes the O-O bond, which eventually breaks heterolytically as water is released and the remaining peroxide oxygen forms a multiple bonds to the iron centre$^{93}$.

This process forms an Fe(IV)=O unit plus a heme radical. The radical quickly undergoes a one electron transfer to move the radical species, leaving the heme ring unaltered. During the second stage, in a similar two electron transfer reaction, Fe(IV)=O reacts with a second hydrogen peroxide to regenerate the original Fe$^\text{III}$ porphyrin, another water molecule and a mole of molecular oxygen. The efficiency of catalase may in part be due to the interaction of His74 and Asn147 with the reaction intermediates$^{89}$.

Another subclass of enzymes, known as catalase-peroxidase enzymes (KatGs,) are bi-functional enzymes that have both catalase and peroxidase activities. In fact both peroxidase and catalase reactivity channels often compete within a single enzyme. Horseradish peroxidase for example exhibits catalase like behavior in the presence of iodide or hydrogen peroxide and in the absence of substrates$^{94}$.
KatGs and monofunctional peroxidases have a similar structural architecture. The proximal and distal heme pockets contain conserved amino acids at almost identical positions as in other Class I peroxidases, such as cytochrome C peroxidase and ascorbate peroxidase.

In KatGs, the heme is deeply buried in the protein and the channel is longer and more restricted than in mono-functional peroxidases. To give catalase activity to the peroxidase core, it has been found that aspartic acid (situated in the heme distal cavity at the main access channel entrance) and a cross-linked adduct formed by tryptophan, tyrosine, and methionine (and also arginine) are required, which are unique to KatGs. There are disparities in the reaction kinetics between KatGs and mono-functional enzymes. Mono-functional catalases and peroxidases display much faster reaction rates and are active over a broad pH range, whereas KatG activities are limited to relatively narrow pH ranges that differ for the catalase and peroxidase activities. The maximum peroxidase activity takes place at pH 4.5 (in Burkholderia pseudomallei, BpKatG) while the maximum catalase activity occurs at a more neutral pH of 6.5 in (BpKatG).

It has been historically assumed that the catalytic mechanism of KatGs was similar to that of mono-functional catalases. However, recent stop-flow spectroscopy studies of KatGs revealed spectral characteristics not previously seen in mono-functional catalases. This suggests that KatGs follow a different catalytic reaction pathway. Current research is focused on finding the electronic and structural basis of this bi-functionality to finally distinguish the switch between catalase and peroxidase activities. KatGs are associated with NADH oxidase, INH lyase, and isonicotinoyl-NAD synthase activities.

1.3.6 Other metal complex activation of hydrogen peroxide

There are many different transition metal catalysts that have been developed which undergo oxidation reactions with a number of oxidants and a variety of substrates. Nevertheless, only metal complex activation of hydrogen peroxide is discussed below.

One class of compounds that catalytically activate hydrogen peroxide is the polyoxometallates (POMs) which are defined as metal-oxygen anionic clusters that can function as multidentate, totally inorganic and oxidatively resistant ligands for redox-active ions. POMs have acidities, redox potentials, solubility and other molecular properties that can be systematically altered. In addition, the delocalized nature of the molecular orbitals in POMs renders them highly...
effective $\pi$-acceptor ligands. These anions can function as multi-electron oxidants whose redox properties can be controlled by alteration of their compositions (the reduced forms are often called heteropoly blues on account of their intense colours). They are remarkably stable both in the solid phase and in aqueous solution, making them useable as heterogeneous and homogenous catalysts$^{101}$. POMs for $\text{H}_2\text{O}_2$-based oxidations can be categorized into three main groups; di and tetranuclear small peroxotungstates, lacunarypolyoxotungstates and transition metal-substituted POMs$^{102}$. Recent studies on the catalyst design of POMs showed that various POMs and peroxotungstate could be used as effective catalysts for selective oxygen transfer reactions, such as epoxidation, sulfoxidation, and Baeyer–Villiger oxidation. The high efficiency of $\text{H}_2\text{O}_2$ utilization, which means that negligible decomposition of $\text{H}_2\text{O}_2$ occurs to form molecular oxygen leads to the simple, efficient, and safe oxidation processes$^{102}$.

Small peroxotungstates such as $[\text{PO}_4\{\text{WO(O}_2)_{2}\}_4]^{3-}$ and $[[\text{WO(O}_2)_2(\text{H}_2\text{O})_2](\mu-\text{O})]^{2-}$ can catalyze the oxidation of various organic substances$^{103,104}$ while lacunarypolyoxotungstates can act as catalyst precursors of polynuclearperoxo species due to vacant sites which can be activated by hydrogen peroxide, for example tetraperoxo species, $[\beta_3-\text{Co}^{II}\text{W}_{11}\text{O}_{35}(\text{O}_2)_4]^{10-}$. This species shows specific reactivity and selectivity due to its unique electronic and structural character. Lacunary POMs are most often used as precursors of transition-metal substituted POMs. The oxo-ligands at the vacant sites readily react with various kinds of transition metal cations$^{102}$. Examples of (POM) structures are shown in Figure 17:
Figure 17: Selected types of polyoxometallates
1.3.6.1 Metalloporphyrin

Recently reported in the literature was the first enantioselective asymmetric catalytic oxidation of sulfides by using a chiral water soluble iron porphyrin with hydrogen peroxide, this reaction yielded optically active sulfoxides in very high enantiomeric excess (up to 90%)\textsuperscript{105}. The water-soluble iron porphyrin that was used is shown in Figure 18. It was prepared by modification of a previously reported optically active porphyrin, by incorporating four sulfonate groups. This porphyrin was originally designed by R. L. Halterman and S. T. Jan to undergo asymmetric epoxidation of unfunctionalised alkenes, incorporating a manganese metal centre and using stoichiometric amounts of commercial bleach as the oxidant\textsuperscript{106}.

![Figure 18: A chiral water soluble iron porphyrin](image-url)
1.3.6.2 Biscyclam

A series of tetraaza and pentaaza cross bridged macrocyclic ligands have been studied as hydrogen peroxide activators. Complexes formed through metallation of a ligand called biscyclam (Figure 19) with manganese (II) and iron (II) has been shown to exhibit a high level of hydrolytic stability in both basic and acidic solutions\textsuperscript{107}. The complexes also undergo rapid exchange of the axial chloride ligands for aqua ligands in aqueous solution. Detailed mechanistic studies have not been undertaken, however studies involving EPR sensitive radical trapping has shown that the hydroperoxyl radical is formed and no high valent metal-oxo species were observed\textsuperscript{108}.

![Figure 19: A tetraaza macrocyclic ligand referred to as biscyclam](image)

It has been reported that manganese salts activate hydrogen peroxide in detergent that contains sodium carbonate with reasonable success, however staining of the fabrics occurs due to the build-up of the manganese oxide\textsuperscript{109}. It has also been reported that manganese salts in bicarbonate solutions activate hydrogen peroxide and catalyse the epoxidation of alkenes\textsuperscript{110}.

A dinuclear manganese compound containing 1, 4, 7-trimethyl-1, 4, 7-triazacyclononane (Me\textsubscript{3}tacn)\textsuperscript{111} ligands has been more successful as a detergent based bleaching catalyst. The exact mechanism for oxidation is not fully known, however both the di-nuclear and mono-nuclear LMn\textsuperscript{V}=O species are believed to be the active oxidant species. There has been debate about which is the active species, a manganese-oxo species or hydroxyl radicals. A study showing the reactivity of [Mn\textsuperscript{IV}(\mu-O)-(Me\textsubscript{3}tacn)\textsubscript{2}]\textsuperscript{2+} (Figure 20) and H\textsubscript{2}O\textsubscript{2} for the oxidation of catechol in the absence and presence of mannitol found that the quinine formed degrades faster in the absence of mannitol than in the presence of mannitol. The researchers therefore postulated that hydroxyl radicals were formed and these were therefore responsible for the
oxidation\textsuperscript{112}. However EPR studies were not carried out to further support this theory and in fact another study involving EPR-sensitive spin traps did not indicate that hydroxyl radicals were formed\textsuperscript{113}.

Schiff-base ligands containing manganese centres have also been investigated for stain bleaching and dye–transfer inhibition\textsuperscript{111}. These catalysts activate hydrogen peroxide although they are less efficient catalysts that the Mn-Me\textsubscript{3}tacn complexes. However, they do not effect fabric dye-fading to the same extent and the complexes are easier to synthesize. Again, a Mn\textsuperscript{V}=O intermediate is postulated as the active oxidation species\textsuperscript{114}. The Jacobsen catalysts\textsuperscript{115} and the related Katsuki catalyst\textsuperscript{116} are commonly used for asymmetric epoxidation reactions of cis-olefins. The terminal metal oxo active oxidant is typically formed by using oxidants such as NaOCl where turn-over number values are in the range of 35-40. Hydrogen peroxide is less commonly used as the oxidant with varying results, often requiring a co-catalyst such as carboxylate salts\textsuperscript{117}. Examples of Schiff base-ligands can be seen in Figure 21 below:

Figure 20: Dinuclear-Mn–Me\textsubscript{3}tacn catalyst. Me\textsubscript{3}tacn=1,4,7-trimethyl-1,4,7 triazacyclononane
Figure 21: Examples of Schiff-base ligands, which together with manganese have been patented as bleaching catalysts.
1.4 Homogenous and heterogeneous catalysis

In general, catalysts can be categorized into two major groups, homogeneous and heterogeneous catalysts. This distinction is linked by the fact that the catalyst operates either in the same phase where the reaction occurs (homogeneous catalysts) or in a different phase (heterogeneous catalysts)\textsuperscript{118}. For homogeneous catalysis, most of the reactions take place in the liquid phase while for heterogeneous catalysis, the catalyst normally exists in the solid phase and the reaction occurs either in the liquid or gaseous phase\textsuperscript{118}. The fact that the catalyst is in a different phase with respect to the reaction medium offers many advantages as summarized in Table 6 below:

<table>
<thead>
<tr>
<th>Properties</th>
<th>Homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst recovery</td>
<td>Difficult and expensive</td>
<td>Easy and Cheap</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Excellent/Good- single active site</td>
<td>Good/poor-multiple active site</td>
</tr>
</tbody>
</table>

Table 6: Comparison between homogenous and heterogeneous catalysis

Even though heterogeneous catalysts have greater advantages with respect to facile catalyst recovery\textsuperscript{119}, recycling and good thermal stability, homogeneous catalysts exhibit superior advantages regarding selectivity. In homogeneous catalysts, every single catalytic entity can act as a single active site which makes the reaction intrinsically more active and selective compared to traditional heterogeneous catalysts such as oxides or supported metal particles\textsuperscript{1}. In addition, it is often possible to tune the chemo-selectivity, regioselectivity and/or enantioselectivity of homogeneous catalysts.\textsuperscript{120}
1.4.1 Types of heterogeneous catalyst in general
Different strategies have been used to immobilize redox-active elements in a solid (inorganic) matrix (Figure 22). Firstly metal ions can be isomorphously substituted in the framework positions of molecular sieves, for example zeolites, silicates and aluminophosphates (APOs)\textsuperscript{121,122}.

![Figure 22: Schematic representation of strategies for heterogenization of metal centre (M)](image)

The range of substrate molecules that are amenable to catalysis by molecular sieve materials was considerably expanded by the discovery, in 1992, of mesoporous (alumina) silicates such as MCM-41\textsuperscript{123}.

Secondly amorphous mixed oxides can be formed by grafting of metal compounds onto the surface, for example silica\textsuperscript{124} or by the sol-gel method\textsuperscript{125}. The latter is equivalent to the hydrothermal synthesis of molecular sieves (but without template) and can afford much higher levels of incorporation than the grafting technique. For example, grafting techniques result in the incorporation of ca. 2% titanium in silica while titania-silica aerogels or xerogels typically contain up to 20% titanium\textsuperscript{126}.
In addition, metal complexes can be tethered to the surface of a solid support, for example with silica, via a spacer ligand. Similarly, coordination complexes or organometallic species can be grafted or tethered to the internal surface of mesoporous molecular sieves. Examples include the synthesis of surface-grafted Ti-(IV)\textsuperscript{127} and oxomanganese\textsuperscript{128}.

Another approach is to encapsulate metal complexes in solid matrices. For example, the so-called ship-in-a-bottle concept, which involves the entrapment of a bulky complex in a zeolite cage, has been widely used to immobilize metal complexes of phthalocyanines, bipyridyls, and Schiff’s base type ligands\textsuperscript{129,130}. Metal complexes can also be heterogenized by encapsulation in polydimethylsiloxane membranes\textsuperscript{129} or by attachment to oxidatively resistant organic polymers such as polybenzimidazole\textsuperscript{131}.

In a separate study it was found that metal ions can be immobilized by cation exchange into zeolites or acidic clays and oxoanions such as molybdate and tungstate can be exchanged into hydrotalcite-like anionic clays (so-called layered double hydroxides, LDHs)\textsuperscript{123}. A major disadvantage is the mobility of the metal ion which manifests itself in its facile leaching into solution\textsuperscript{121}.

### 1.4.2 Amino Groups Immobilized on Silica Gel: an Efficient and Reusable Heterogeneous Catalyst for the Knoevenagel Condensation

The Knoevenagel reaction involves the condensation of a carbonyl compound with compounds containing a methylene group activated by one or two electron-withdrawing substituents, such as nitrile, acyl and nitro. Several heterogeneous catalyst systems have been reported to be successful for this reaction. For instance the Knoevenagel reaction using aluminium oxide\textsuperscript{132}, xonotline alone or doped with potassium t-butoxide\textsuperscript{133}, molecular sieves\textsuperscript{134} and recently amino groups immobilized on silica gel\textsuperscript{133}. This recent amino group immobilized catalyst system (shown below) was tested for this Knoevenagel reaction using a wide range of compounds including aldehydes, ethyl cyanoacetate and malononitrile according to Equation 13\textsuperscript{133}.

![Catalyst system](image)

Figure 23: Catalyst system
Result show that aldehydes condensed with complete conversion and good yield with ethyl cyanoacetate and malononitrile while diminishing activities were obtained in the order ethyl acetoacetate > ethyl benzoylacetate > acetylacetone. This suggest that the matrix itself is not inert toward reacting species and the result may be explained by the existence of residual free silanol groups in the silica gel that may either activate the carbonyl compound or promote the dehydration of aldol.

Overall, using this heterogeneous system not only allows for easy dehydration of the aldol intermediate but also allows the reaction to be conducted in continuous flow conditions and reduced activity of those methylene compounds that can be adsorbed in enolic form on the matrix surface. The mechanism of action summarised below in Figure 24:
Figure 24: Curved lines represent the surface of silica gel containing silanol groups and immobilized amino functions, dotted lines indicate breaking and forming bonds.
1.4.3 Fabrication of hollow silica spheres with adsorbed Pd for Suzuki Coupling

Another example of the successful application of heterogeneous catalyst is involves the use of hollow silica spheres with adsorbed Pd as a recyclable heterogeneous catalyst for tailored Suzuki coupling reactions\textsuperscript{135}. This system was used with the idea that heterogeneous catalysis provides more advantageous attributes than homogenous especially in term of catalyst recyclability and ease of separation from reaction mixtures.

This novel heterogeneous catalyst was tested using a Suzuki coupling reaction involving iodothiophene and phenylboronic acid. The cross coupling reaction was carried out using 3 mol\% Pd in ethanol as illustrated in Figure 25.

![Figure 25: Suzuki Coupling reaction with iodothiophene and phenylboronic acid](image)

The result showed that not only are the hollow silica spheres with adsorbed Pd active for this reaction but in addition the catalyst can be recycled up to 7 times without losing its catalytic activity\textsuperscript{136}. Furthermore there is no leaching associated with this system which is important when the Pd catalyst is used for pharmaceutical production. Moreover, the catalyst can be easily recovered by simple filtration.
1.4.4 Supported Ruthenium Catalyst for the Heterogeneous Oxidation of Alcohols with Molecular Oxygen

Other application of a heterogeneous catalytic system can be observed in studies involves ruthenium supported on alumina. Typically, in the past the oxidation of alcohol was carried out non-catalytically with stoichiometric oxidants such as dichromate and permanganate. However, this approach produces a huge amount of metal salts as wastes. Efforts to find heterogeneous catalytic systems resulted in the discovery of an effective aerobic process for the oxidation of both activated and non-activated alcohols. This particular process uses molecular oxygen or air catalysed by Ru supported on alumina (Ru/Al₂O₃) as shown in Figure 26 below:

![Figure 26: General oxidation of supported Ru catalyst with solvent](image)

The Ru/Al₂O₃ catalyst has high activity for the oxidation of both activated or non-activated alcohols using only 1 atm of oxygen. No leaching can be observed throughout experiments and this system can be reused for up to 7 times without loss in activity.

Solvent free heterogeneous oxidations of alcohols on the other hand are more suitable for industrial scale reactions. The Ru/Al₂O₃ catalyst system efficiently facilitated the oxidation of non-activated 2-octanol and activated 1-phenylethanol without the use of solvents. The solvent-free oxidation of 2-octanol, and 1-phenylethanol at 423 K had turn over frequencies (TOFs) of 300 h⁻¹ and 340 h⁻¹, and TONs of 950 and 980, respectively (Figure 27). These TOFs and TONs are higher than those reported for the aerobic oxidation of 2-octanol by other Ru catalysts.
As discussed above, no ideal process has been developed so far for general industrial oxidation reactions and in particular for water treatment and purification. One of the most promising areas is the use of advanced oxidation processes (AOPs) in conjunction with hydrogen peroxide as the oxidant. However, all the technologies/treatments developed so far suffer from some drawbacks. The homogeneous Fe-TAML(FeB*) oxidation catalysts perform extremely well with hydrogen peroxide as the oxidant, but the requirement for the water being purified to be dosed with catalyst, base and peroxide when operating in homogeneous mode means they cannot be used in practice in this way for water purification. Therefore, to overcome these fundamental problems there was a need to design and develop a novel system in which homogeneous oxidation catalysts such as Fe-TAMLs could be used for water purification without having to add peroxide, catalyst or base to the water being purified. The research described in this thesis achieves this important goal. Smart catalytic films were developed that enable homogeneous catalysts to be used for water purification without contamination of the water with oxidants or catalysts.

![Figure 27: Oxidation of 2-octanol and 1-phenylethanol using Ru/Al₂O₃ in solvent free conditions](image)
1.5 Catalyst Introduction

In general, there is a variety of anionic catalysts that can be used in conjunction with the system that was developed. However, the catalyst of primary interest was the iron-(TAML) FeB* because of its outstanding features and remarkable catalytic characteristics in homogenous systems. Among the attractive features of this catalyst are: its relatively simple preparation, its high water solubility and its very high activity. Since this catalyst will dominate most of the systems discussed, an in-depth study of the catalyst is given in section 1.5.1.

1.5.1 Design and Development of Fe-TAMLs catalyst

In principle, two important features of an efficient catalyst for hydrogen peroxide oxidations are that it is both hydrolytically and oxidatively robust. The design of Fe-TAML catalysts was bio-inspired. Natural oxidation catalysts such as cytochrome P450 and horseradish peroxidise have modified heme groups at the active sites. Therefore, important features that were initially incorporated into the design of Fe-TAML catalysts were a tetradentate, N-donor ligand set that was oxidatively resistant\(^\text{139}\). However, in order to produce an efficient catalytic peroxide system, one needs to avoid Fenton chemistry that often occurs, especially when simple ferric or ferrous iron interacts with the hydrogen peroxide\(^\text{140}\) in water. Even though Fenton chemistry produces highly oxidising hydroxyl radicals, as has been discussed above Fenton chemistry is undesirable because it is a non-selective, inefficient process that ideally operates in acidic solution and produces a large amount of waste\(^\text{141}\). The Fe-TAML catalysts do not produce hydroxyl radicals, but instead, on interaction with hydrogen peroxide, a very strongly oxidising terminal iron-oxo species is formed. This terminal metal-oxo complex is formed when a single catalytic metal ion abstracts an oxygen atom from hydrogen peroxide and discards water, making the two-electron oxidized metal-oxo species\(^\text{141}\). The design and development process for Fe-TAMLs from 1980 up to 2000 is shown below in Figure 28:
The precursors of TAML ligands started with the ligand systems known as polyanionic chelating ligands (PACs). These PAC ligand systems contain two deprotonated amide nitrogen donors and two deprotonated –OH donors as shown in Figure 29 below. These ligands undergo a metallation process to form complexes with first row transition metal such as Co, Cr, Cu and Fe$^{142}$. The ligand systems are able to stabilize metals in higher oxidation states and can act as catalysts with low activity for hydrogen peroxide oxidations of organic substrates.
Even though a wide range of transition metals have been incorporated within the PAC structure, none have been shown to be powerful and efficient oxidation catalysts.

The formation of macrocycles was not possible with these polyanionic ligands with 2 nitrogen and 2 oxygen donors as the valency limitation of the negatively charged oxygen donors makes macrocycle formation impossible. Nitrogen does not have these limitations and so, the design of the ligand progressed to replace the two oxygen donors with two amide nitrogen donors. A square planar ligand of the correct size should be very favourable for coordination to a transition metal ion because of the macrocyclic effect. It also leaves one or two coordination sites on the metal ion available for coordination and activation for hydrogen peroxide\(^{143}\). The advance to the tetraamido ligand system was also driven by the fact that the metallated PAC ligands were found to undergo significant hydrolysis, and that they were susceptible to oxidative degradation.

In this way further ligand modification was achieved through the iterative development process described above with the goal of synthesizing ligands that would be more effective as oxidation catalysts. The type of ligand system that has been utilized by the Collins group more recently has been based around what is termed a “non-innocent” ligand. This is because the oxidation state of the coordinated ligand is not always well defined as the phenylenediamido-N-unit of the ligand can undergo redox reactions in addition to the metal\(^{141}\). One of the most significant developments of the Fe-TAML design process came in 1994. During the design process, it was discovered that the di-ethyl Fe-TAML slowly degraded under oxidative conditions to produce a hydantoin-containing product (Figure 30). This product is formed by hydrogen atom

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**Figure 29 : Basic PAC ligand and complex structures**

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abstraction from the methylene position of the ethyl group by the active Fe-(V)=O intermediate. In principle, this process can proceed either via intra or intermolecular abstraction.

In the event of low catalyst concentration (µM) and high substrate concentration (mM), the hydrogen atom abstraction proceeds mostly via an intramolecular oxidation mechanism. A significant experiment was undertaken where the bleaching of an easy to oxidize dye, pinacyanol chloride, caused by the diethyl-TAML and dimethyl-TAML iron complexes was measured over time. The dimethyl-TAML catalyst (Li₂Fe(Cl)B*) was shown to have a significantly longer lifetime than the diethyl-TAML complex which degrade rapidly under the conditions used. The C-H bond strength of this “tail” region of the ligand can be increased by approximately 3 kcal mol⁻¹ by replacing the two ethyl groups with methyl groups.

The results of this dye oxidation experiment confirmed that with the methyl groups on the ligand, the oxidative stability of the complex is substantially increased and therefore it was reasonable to assume that the abstraction of the hydrogen atom was the source of the rapid degradation of the diethyl complex.³⁴ Further substitution of the macrocycle has led to other significant increases in stability since this breakthrough in 1994. Electron withdrawing groups on the methylene carbon of the tail region of the complex has led to increased hydrolytic stability. A di-fluorinated complex, Li₂Fe(Cl)B*(F₂) (Figure 31) is stable in a solution at pH 3 for months and is five orders of magnitude more stable to H⁺ demetallation in the weakly coordinating, strong acid, HClO₄. The tail amide oxygen atoms are sites for protonation and so substituting the methyl groups of Li₂Fe(Cl)B* with electron-withdrawing fluorine groups reduces the rate of hydrolytic demetallation (Figure 31).

![Figure 30: Diethyl Fe-TAML complex and its hydantoin degradation product](image)
Electron withdrawing groups such as NO₂ on the benzene ring increase the rate of formation of the reactive iron-oxo intermediate species\textsuperscript{146}. Moreover the introduction of charged substituents on the benzene ring of the ligand alters the overall charge of the complex.
1.5.2 Synthesis of Fe-TAMLs

The synthesis of the H$_4$B$^*$ ligand system has undergone considerable modification in order to achieve more efficient and safer methods of production. These advances provide advantages in term of elimination of intermediate organodiazides during the reaction$^{147}$. The current method incorporates the addition of $\alpha$-aminoisobutyric acid to different dianinobenzenes. This forms an intermediate that, on addition of an acid chloride such as dimethylmalonyl dichloride, forms the tetraamido macrocycle$^{148}$.

The details are provided in the reaction scheme illustrated in Figure 32. Phthalic anhydride and $\alpha$-amino isobutyric acid are fused together to form 2-methyl-2-phthalimidopropanoic acid. Then thionyl chloride was added to produce 2-methyl-2-phthalimidopropanoyl chloride. A THF solution of o-phenylene diamine and triethylamine is added dropwise to a THF solution of 2-methyl-2-phthalimidopropanoyl chloride and a pale brown solid, the phthalimido-protected diamide diamine is then formed. This was added to dry ethanol along with hydrazine dihydrochloride and NEt$_3$ to form the diamide diamine (see Figure 32). The diamide diamine was added to a solution of dimethylmalonyl chloride and this gave rise to the macrocyclic tetraamide ligand. The final yield of the ligand was approximately 55%$^{149}$. 
Figure 32: General synthesis of the tetraamide macrocyclic ligand, TAMLs

Metal insertion into the TAML ligand is carried out after the production of the ligand system (Figure 33). The amide nitrogen atoms of the ligand are deprotonated using a suitable base,
followed by the coordination of the iron to the ligand. Initially, the most commonly used base was t-BuLi, with FeCl₂ used to metallate the ligand. This was then oxidised by air to the Fe-(III)-TAML complex. As BuLi has associated practical application problems, other bases are now preferred, such as KOT-Bu or lithium bis(trimethylsilyl)amide and FeCl₃ is used in place of FeCl₂.

**Figure 33: Metallation of the tetraamido macrocycle with KOT-Bu and FeCl₃**

The metallated Fe-TAML complex can be separated as a salt with various different counter cations. With butyl lithium acting as a base, the lithium salt is initially obtained. Changing the counter cation can alter the solubility of the Fe-TAML complex, which eventually affects the chemical properties. Conversion to a tetraethyl ammonium salt can be achieved by using a cation exchange column. Converting to a tetraphenylphosphonium salt was achieved by adding a solution of PPh₄Cl in water to a solution of Li₂Fe(Cl)B* in water. The [PPh₄][Fe(H₂O)B*] salt precipitates out of the water and can then recrystallised from acetonitrile/water. This Fe-TAML complex is subsequently soluble in organic solvents, such as dichloromethane (DCM).
1.5.3 Crystal Structure of Fe-TAMLs [Net₄][FeB*(Cl)] catalysts

In the solid state, [Net₄][FeB*Cl₂(H₂O)] exhibits a five coordination geometry, with one axial chloride ligand. The iron centre sits slightly out of the plane defined by the four amidate donors, towards the axial ligand. The crystal structure of the complex is shown in Figure 34 below:

![Crystal Structure of [Net₄][FeB*Cl₂(H₂O)]](image)

The average Fe-N distance is 1.898 (3) Å. The central iron atom sits out of the plane of the four nitrogen atoms by a distance of 0.363 (1) Å. In aqueous solution, a water ligand coordinate to the metal centre in each of the axial positions, replacing the chloride ligand and this results in an octahedral structure.
1.5.4 General properties of Fe-TAMLs

X-ray structures of [Fe(H₂O)B*]⁺ and [Fe(Cl)B*(F₂)]²⁻ show that in the solid state Fe-TAMLs complexes are five-coordinate species. Normally, Fe-TAML complexes have either Cl or H₂O as the axial ligand in the solid state. The ligand has a relatively high degree of planarity with all the amide nitrogens lying in the same plane and the iron located slightly out of the amide plane towards the axial ligand. Solution based EPR studies of [Fe(H₂O)B*]⁺ show that Fe-TAMLs become six-coordinated species in water. The spectrum of a powdered sample of [Fe(H₂O)B*]-, at 13 K where the fifth axial ligand is a water molecule, exhibits two sets of g-values of 5.6, 1.8, 1.3 and 5.4, 2.3, 1.6 due to the two doublets (m = ±3/2 and ±1/2 respectively), of spin S= 3/2 rhombic Fe(III)-TAML complex. The axial and rhombic parameter are D = -1.6(2) cm⁻¹ and E/D = 0.29. When dissolved in water at pH 7, the complex gives g values of 4.0 and 2.0 which are characteristic for a S=3/2 complex with axial symmetry, E/D =0. The temperature dependence of the signal indicates a positive D value of +2 cm⁻¹. The change in the axial and rhombic parameters suggests that once dissolved in water, a second water molecule coordinates to the iron and occupies the sixth axial position. Gas phase DFT calculations support the EPR studies and these show that when the Fe-TAML was dissolved in water, a six-coordinate Fe(III)-TAML complex was more energetically favourable than five-coordinate analogues. EPR and UV-Vis data suggested that [Fe(H₂O)B*]- and other related Fe(III)-TAML complexes at higher pH form iron species with OH and H₂O as axial ligands, resulting from the removal of a proton from one of the axial water molecules. The EPR spectra of the Fe-TAML complex, [Fe(Cl)(Cl₂B*)]²⁻ at pH 10 shows a g value of 4.6 which is characteristic of an S= 3/2.
1.5.5 Application of Fe-TAMLs in general

Fe-TAML catalysts work efficiently in conjunction with hydrogen peroxide to make an oxidizing system that may be able to eliminate the use of chlorine-based bleaches. This would be a huge advantage especially in the pulp and paper bleaching industry. Chlorine-based bleaching reagents such as ClO₂ are currently used because they have high selectivity for lignin and are reasonably inexpensive. However, these reagents create several drawbacks such as producing toxic chlorinated organic waste, and have relatively high energy and water usage. This problem may be overcome in the future by using Fe-TAML technologies in conjugation with H₂O₂ in a new oxidation system. Successful Fe-TAML applications may also be found in the future in other fields such as in the oxidative treatment of industrial waste streams, removal of hazardous dyes and pesticides from water, the oxidation of sulfur-containing compounds (such as thiophene) in crude oil to facilitate their removal and significantly reduce colour and smell from the wastewater generated by paper mills and greener synthesis of commodity and specialty chemicals.

1.5.5.1 Degradation of environmentally persistent chemicals

Several persistent complexes such as chlorophenol, nitrophenol and trinitrotoluene have been shown to undergo complete degradation using the Fe-TAML/hydrogen peroxide oxidation system. Since some organophosphorus pesticides can exhibit acute neurotoxicity, several procedures have in the past been implemented to treat compounds of this type but these normally resulted in the formation of harmful by-products. Nevertheless, Fe-TAML catalysts have the ability to completely degrade Fenitrothion (Figure 35) in aqueous media with hydrogen peroxide as the oxidant.

![Fenitrothion](image)

Figure 35: The organophosphorus pesticide fenitrothion
Under ambient conditions, Fenitrothion was completely converted to 3-methyl-4-nitrophenol. This was followed by 95-98% degradation of the 3-methyl-4-nitrophenol to form small aliphatic acids with no sign of Fenitrothion. This degradation was also observed with the other major, organophosphorus pesticides and parathion. Chlorophenols have been used in various applications such as pesticides, wood preservatives and disinfectants. There is a growing concern regarding the toxicity and environmental effects of chlorophenols resulting in the regulation of a number of these compounds. Recently several techniques have been investigated to degrade chlorophenols, with varying results. Biological methods are slow and ineffective at high substrate concentrations and in fact form toxic by-products, for instance polychlorinated dibenzo-p-dioxins and dibenzofurans. Synthetic degradation methods have also been investigated, with the most effective method utilizing hydrogen peroxide catalysed by water-soluble ironphthalocyanines. However, this method produces a significant percentage of chlorinated organic materials in the degradation products.

![Pentachlorophenol](image1)

![2,4,6-trichlorophenol](image2)

*Figure 36: Two examples of chlorophenols, TCP and PCP*

Fe-TAML complexes have been shown to rapidly oxidize the chlorophenols 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) under ambient conditions (Figure 36). Importantly, no dioxins or any other toxic compounds were detected in the products.

1.5.5.2 Decolourization of Textile Effluent Streams

The textile industry faces the continuing challenge of removing the organic and the colour content from their wastewater. As with the pulp and paper industry, organic and highly coloured chemical species cause environmental problems for the water systems they are released into. Typical treatment technologies prior to wastewater release include oxidation, biological and photo-degradation of the colour and organic content. Hydrogen peroxide is employed as one of the chemical methods for wastewater decolourization and often is used in
conjunction with transition-metal catalysts or Fenton reagents. However, the limitations of these current technologies have been discussed above. Hydrogen peroxide activated by Fe-TAML catalysts has been investigated for the successful colour reduction of these waste streams. In some cases, complete colour removal was achieved, although elevated operating temperature was required\textsuperscript{142}.

1.5.5.3 Deactivation of persistent biological spores

Fe-TAML complexes have been shown to effectively and quickly deactivate spores of the bacteria species \textit{Bacillus atrophaeus}. These spores are accepted as being a suitable surrogate for the biological warfare agent \textit{Bacillus anthracis}, which causes anthrax. Bacillus spores are very resistant to enzymatic and chemical degradation. Even though there are disulfide bonds present in the protein spore coat, these are difficult to oxidize\textsuperscript{158}. However, Fe-TAML together with hydrogen peroxide was able to achieve greater than 90% conversion of cysteine to cysteic acid within one hour (pH 10.0, 25.8° C) by oxidizing the disulfide bond of the cysteine. This compared to <5% with hydrogen peroxide alone.

These results show potential of Fe-TAML in conjunction with hydrogen peroxide to oxidize these disulfide bonds. Treating the Bacillus atrophaeus spores in the presence of cetyltrimethylammonium bromide (CTAB, a cationic surfactant) with hydrogen peroxide alone at pH 10.0 gave <2 log kill (99%) of the spores after one hour. Addition of the Fe-TAML complex could achieve a 5log kill (99.9999%) after one hour. Using a less hydrophilic oxidant, t-butylhydroperoxide, along with CTAB achieved a $10^7$ fold decrease (99.99999%) in the active Bacillus atrophaeus spore population in less than 15 minutes, which is the US military standard for effective decontamination\textsuperscript{159}. Since t-butylhydroperoxide is less hydrophilic, greater concentration of the peroxide would occur at the spores. Furthermore, t-butylhydroperoxide is less susceptible to catalase type decomposition than hydrogen peroxide\textsuperscript{160}, which most likely increases the efficiency of the deactivation of the spores.
1.5.5.4 Pulp de-lignifications and wastewater effluent treatment

Chlorine-based oxidation technologies have dominated the pulp and paper industry especially in the production of white paper. The aim of the bleaching process is to remove the final amounts of lignin bound to the cellulose after pulping. The lignin is chemically oxidized and degraded to break it into many different water soluble organic compounds that can be washed away. Before 1960, elemental chlorine was commonly used as the oxidant, but more recently this has been replaced by chlorine dioxide. These chlorine based oxidants produce chlorinated organic by-products, which are regarded as extremely hazardous pollutants.

Other oxidants such as hydrogen peroxide and ozone, are also used, normally in conjunction with chlorine dioxide. However these oxidants are sluggish to react under ambient conditions, have limited selectivity and tend to also oxidize and degrade the cellulose. Fe-TAML catalysts activate hydrogen peroxide to rapidly and selectively bleach wood pulp at room and elevated temperature\textsuperscript{142,161}. Acidic and caustic washes are used to remove the oxidized lignin. The caustic wastewater produced during pulp and paper bleaching manufacture is highly coloured. The coloured material in this wastewater reduces the photic depth of the water, which decreases photosynthetic rates and affects aquatic productivity. Since these current removal technologies are not generally sustainable, new environmentally sustainable treatments are required. The effects on effluent bleaching of variables such as reaction time, pH, concentrations of both the hydrogen peroxide and the catalyst, and temperature were originally investigated and the main Fe-TAML complex investigated was, Na\textsubscript{2}[Fe(Cl)B\textsuperscript{*}]. This gave a set of working conditions where the colour removal from pulp mill effluent stream was maximized. These conditions are listed in Table 7:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration</td>
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<tr>
<td>Hydrogen Peroxide concentration</td>
<td>22 mmol L\textsuperscript{-1}</td>
</tr>
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<tr>
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</tbody>
</table>

Table 7: Conditions used for oxidation of pulp and paper caustic waste water effluent
These conditions reproducibly gave colour removal of 47%. Multiple additions of the catalyst and peroxide were also tested to ascertain the effects on colour removal. However, the addition of extra catalyst resulted in no further significant reduction in colour, suggesting that there were no remaining colour causing compounds that could be oxidized by this system. Other modified Fe-TAML complexes were investigated, however the highest colour removal was seen for the TAML catalyst Na₂[Fe(Cl)B*]. Treatment of the plant effluent streams resulted in significant colour removal, and subsequently pilot plant trials have been undertaken. Further research into the performances of substituted Fe-TAML complexes has more recently been investigated. Derivitisation of the H₄B* framework at the malonamide region of the ligand had shown little or no significant increases in the effectiveness of the Fe-TAML complex to remove colour from the caustic waste water effluent. However, substituents on the aromatic of the macrocycle (an electron withdrawing nitro and positively charged group bound to the aromatic ring by an electron withdrawing amide functional group) had a significant effect on both the rate of colour removal and total colour removal. The three Fe-TAML complexes used in this study are shown in Figure 37.

Much lower concentrations of both the Fe-TAML catalyst and the hydrogen peroxide were required with the modified Fe-TAML catalysts, Na[Fe(H₂O)(NO₂B*)]⁺ and [Fe(H₂O)(+veB*)]. Colour removal as high as 67% was observed in the caustic effluent using these catalysts. A significant finding from this research involved the time taken to achieve 50% colour removal. The new, modified FeB* catalysts were able to achieved 50% colour removal in some cases as quickly as 8 minutes, whereas the original Na[Fe(H₂O)B*]- catalyst required up to 90 minutes to achieve this same level of colour reduction.

As the caustic waste effluent is usually treated at the “end-of-pipe”, where time before release into the environment is short, rapid colour removal is required. The fastest time to reach 50% colour removal for Na[Fe(H₂O)B*]⁻ was up to 90 minutes. Introducing holding tanks so that there is enough time to obtain sufficient colour removal is both costly and time inefficient; therefore the results obtained with the [Fe(H₂O)(+veB*)] and Na[Fe(H₂O)(NO₂B*)]-complexes are promising.
Figure 37: Fe-TAML complexes used to bleach pulp and paper caustic effluent waste water

<table>
<thead>
<tr>
<th>Conditions</th>
<th>[Fe(H₂O)(NO₂B*)]- or [Fe(H₂O)(+veB*)]</th>
<th>Previous [Fe(H₂O)B*]- optimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration</td>
<td>0.5 µmol L⁻¹</td>
<td>2 µmol L⁻¹</td>
</tr>
<tr>
<td>H₂O₂ concentration</td>
<td>5 mmol L⁻¹</td>
<td>22 mmol L⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Temperature</td>
<td>40°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Time</td>
<td>1 hour</td>
<td>4 hours</td>
</tr>
<tr>
<td>Colour Removal</td>
<td>Up to 67%</td>
<td>47%</td>
</tr>
</tbody>
</table>

Table 8: Condition used for optimum oxidation of caustic waste water effluent with second generation Fe-TAML complexes.
1.5.6 Evidence for the Fe\textsuperscript{V} oxidation state

It is common knowledge, that high-valent iron-oxo species are used in many biological systems to carry out a number of oxidation reactions. However, most heme-based species, including the peroxidases enzymes do not obtain the Fe(V) state, instead the active complex for these enzymes is an Fe-(IV) oxo porphyrin-radical-cation species\textsuperscript{164}. TAML ligands are able to stabilize a number of different high valent iron species. This is because the deprotonation of the TAML ligand provides iron with four strong negatively charged amido-N (sigma donor ligands) that are not easily oxidized. For this reason, it has been shown that TAML complexes can form oxo-iron-(V) species when they are treated with an oxygen atom transfer agent, for example hydrogen peroxide.

Such an oxo-compound has been synthesized and identified by the reaction of the Fe\textsuperscript{III}-TAML species with m-chloroperoxybenzoic acid at low temperatures. The existence of such compounds has been verified using optical, electron paramagnetic resonance, Mössbauer, and X-ray absorption spectroscopy, as well as electrospray ionization mass spectrometry, reactivity studies, and density function theory. The details of these can be found in the paper by Tiago et al\textsuperscript{164}. It is plausible that this Fe-(V) species is the active catalytic species for substrate oxidation by peroxides. It could behave as either a two electron oxidant (with or without oxygen transfer) where it is returned in one step to the Fe-(III) state, or a one electron oxidant where it would pass through an Fe-(IV)-oxo intermediate\textsuperscript{165}.

1.5.7 Proposed mechanism of action of Fe-TAMLs catalysts

The catalytic ability of Fe\textsuperscript{III}-TAML catalysts resembles that of oxygen activating enzymes such as peroxidase and catalase\textsuperscript{166}. Both these enzymes catalyse reactions associated with hydrogen peroxide.

The reaction catalyzed by catalase enzymes is given in Equation 1\textsuperscript{167}.

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]

Equation 14: Catalytic decomposition reaction of \text{H}_2\text{O}_2

In designing oxidation catalysts such as Fe\textsuperscript{III}-TAML, this behaviour is to be avoided, as no substrate is oxidised in this process, and the overall process is simply the non-productive
decomposition of hydrogen peroxide to oxygen and water. Peroxidases are a very large group of enzymes, which can be divided into three super-families. These are plant peroxidases, animal peroxidases, and yeast peroxidases. Unlike the catalase enzymes, the peroxidases are able to oxidise a substrate such as a phenol. The mechanism for this is shown in equation 15.

In this mechanism, AH is a reducing substrate while $A^0$ is the corresponding free radical species; it is this activity that is desired in biomimetic oxidation catalysts, such as the Fe$^{III}$-TAML system.

Native peroxidases $+$ $H_2O_2$ $\longrightarrow$ Compound I $+$ $H_2O$

Compound I $+$ AH $\longrightarrow$ Compound II $+$ $A^0$

Compound II $+$ AH $\longrightarrow$ Native peroxidase $+$ $A^0$ $+$ $H_2O$

Equation 15: Reactions for peroxidase action

The Na$_2$[FeB*(Cl)] complex is a homogeneous catalyst that operates in aqueous solution, where it has two axial water ligands. It's speciation in aqueous solution is shown in Figure 38.

If hydrogen peroxide is added to this solution, one molecule will easily replace a water ligand. The peroxide ligand can then quickly rearrange, expelling one oxygen atom and two hydrogen atoms as water. This will leave one oxygen atom attached via a double bond to the iron centre, resulting in the active intermediate. The overall process is shown in Figure 39.
Figure 39: Activation of the iron centre of the [FeB*(OH$_2$)$_2$]$^+$ complex

The large positive charge on the central iron atom makes the oxygen atom electron-deficient, which results in the intermediate being reactive enough to extract electrons from, and in some cases add oxygen to, oxidizable substrates present in the solution, returning it to the Fe (III) oxidation state$^{168}$. The Fe (V) oxidation state of the activated complex is extremely unusual, and evidence for this state will be discussed later. The overall catalytic cycle for these complexes is given in Figure 40.
Figure 40: Overall catalytic cycle for [FeB*(Cl)]³⁻
1.5.8 Deducing rate law for the oxidation of substrates with the Fe$^{III}$-TAML/H$_2$O$_2$ system

A general scheme for the activity of TAML catalysts is given in Figure 41:

\[ \text{Fe}^{III}\text{-TAML} \xrightarrow{k_-} \text{O}_2 \xrightarrow{k_{III}} \text{S(ox)} \xrightarrow{k_1} \text{S(red)} \xrightarrow{k_II} \text{Oxidized-Fe-TAML} \]

Figure 41: Overall process for oxidation by Fe$^{III}$-TAML catalysts

From this, a simple rate law can be derived. This requires several assumptions. Firstly, step III, the catalase activity, is ignored. Also, based on the mass balance equation, [Fe$^{III}$-TAML] is assumed to be the total concentration of all TAML iron species present in solution. Finally, the rate law suggests that the catalytic activity by Fe$^{III}$-TAMLs mimics the steady state oxidation typical of peroxidase enzymes. This results in the rate law given in Equation 16:

\[
\frac{-d[S(red)]}{dt} = \frac{k_1 k_{II} [Fe^{III} - TAML][H_2O_2][S(red)]}{k - k^{-1} + K_I [H_2O_2] + K_{II} [S(red)]}
\]

Equation 16: Rate law for the oxidation of dye by hydrogen peroxide catalysed by Fe$^{III}$-TAML

This rate law has been obtained by extensively studying the oxidation of orange (II) dye at different dye and hydrogen peroxide concentrations. These studies indicate that $k_1$ is negligible, and that the reaction rates reach a plateau with increasing concentration of both reagents. The values of $k_1$ and $k_{II}$ can be calculated by manipulating the reaction conditions. If the concentration of hydrogen peroxide is low, the formation of the oxidised TAML species becomes the rate limiting step, and the reaction rate becomes independent of the orange II concentration, so the rate law can be written as (Equation 17):
\[-\frac{d[S_{\text{red}}]}{dt} = k_{II} [Fe - TAML][S_{\text{red}}] \]

**Equation 17:** Simplified rate law when the hydrogen peroxide concentration is low, so step I is rate limiting

Alternatively, if the concentration of hydrogen peroxide is high, then the formation of the oxidised TAML species becomes fast, so the oxidation moves into a different kinetic regime, where the oxidation of the dye becomes the slow step, so the rate law can be written as (Equation 18):

\[-\frac{d[S_{\text{red}}]}{dt} = k_{II} [Fe - TAML][S_{\text{red}}] \]

**Equation 18:** Simplified rate law when hydrogen peroxide concentration is high, so step II is rate limiting

At pH 11, and 25°C, the values of \( k_{I} \) and \( k_{II} \) have been found to be \( 3.5 \times 10^{3} \) and \( 1.5 \times 10^{4} \) mol L\(^{-1}\) s\(^{-1}\) respectively\(^{165} \). This indicates that that the catalyst has a high activity especially with respect to \( k_{II} \). The kinetic behaviour of [FeB*(Cl)]\(^2\) and other Fe\(^{III}\)-TAML catalysts resembles simple **Michealis Menten kinetics**, with respect to the concentration of hydrogen peroxide. The simplest form of Michealis Menten enzyme kinetics can be expressed by the following reaction (Equation 19)

\[
E + S \rightleftharpoons_{k_{-1a}}^{k_{1a}} ES \rightarrow_{k_{1b}} E + P
\]

**Equation 19:** General scheme for Michealis Menten enzyme kinetics

Here, \( S \) is the hydrogen peroxide, and \( E \) is the [FeB*(Cl)]\(^2\) catalyst. The \( k_{1a}, k_{-1a}, \) and \( k_{1b} \) are equivalent to the rate constants \( k_{I}, k_{I}, \) and \( k_{II} \) respectively. For this scheme to be applicable, the concentration of the Fe\(^{III}\)-TAML must be much less than that of hydrogen peroxide, so that the Fe\(^{III}\)-TAML concentration becomes the rate limiting factor\(^{169} \). Other necessary assumptions are the steady state assumption, that the concentration of Fe\(^{III}\)-TAML is constant throughout the reaction, that the reverse reaction is negligible, and that the product formed does not inhibit the catalyst\(^{169} \).
Through these assumptions, the following rate law can be derived (Equation 20), where \( v \) is the initial rate of the reaction, and \( K_M \) is the Michaelis Menten constant:

\[
v = \frac{[H_2O_2]^{2/2}}{[H_2O_2] + K_M}
\]

Where,

\[
K_M = \frac{k_{-1} + k_{ii}}{k_i}
\]

Equation 20: Rate law for Michaelis Menten enzyme kinetics

By plotting \( 1/[H_2O_2] \) against \( 1/\text{initial rate} \), in what is known as a Lineweaver-Burk plot, the values of \( K_M \) and \( v_{\text{max}} \) can be derived from the slope and y-intercept.

1.5.9 pH dependence of catalysis by Fe\textsuperscript{III}-TAMLs

The activity of the Fe\textsuperscript{III}-TAML catalysts is highly dependent on pH. The pH profile at different temperatures for the rate of dye bleaching by hydrogen peroxide and [FeB\textsuperscript{6}(Cl)]\textsuperscript{2-} is given in Figure 42:\textsuperscript{159}

![Figure 42: Dependence of K\textsubscript{Obs} on pH, for the Fe-TAML catalyst [Fe(OH\textsubscript{2})(B\textsuperscript{6} Cl)]\textsuperscript{2-}, conditions: [Fe-TAML]=1.28 x 10\textsuperscript{-7} mol L\textsuperscript{-1}, [orange II]=5.81 x 10\textsuperscript{-5} mol L\textsuperscript{-1}, and [H\textsubscript{2}O\textsubscript{2}]=3.3 x 10\textsuperscript{-4} mol L\textsuperscript{-1}, in a 0.01 mol L\textsuperscript{-1} phosphate buffer.](image)
The rate constant reaches a maximum value around pH 10. This behaviour can be rationalised by the scheme given in Figure 43\textsuperscript{159}.

\[ \text{[FeB*(OH\textsubscript{2})\textsubscript{2}]^+} \overset{k_{a1}}{\rightleftharpoons} \text{[FeB*(OH)(OH)]\textsuperscript{2-} + H^+} \]

\[ \text{ROOH} \overset{k_{a2}}{\rightleftharpoons} \text{ROO^- + H^+} \]

\[ k_j [H^+]^2 + (k_2 K_{al} + k_3 K_{a2}) [H^+] + k_a K_{al} K_{a2} \]

\[ k_{obs} = \frac{k_j [H^+]^2 + (k_2 K_{al} + k_3 K_{a2}) [H^+] + k_a K_{al} K_{a2}}{[H^+]^2 + (K_{al} + K_{a2}) [H^+] + K_{al} K_{a2}} \]

\textit{Equation 21: Calculation for k dependence on pH}

From Equation 21, it is clear that the value for the rate constant will depend on the pH of the solution. This is further justified by certain characteristics of the deprotonated and protonated species. For example, the deprotonated version of the Fe\textsuperscript{III}-TAML complex is more electron rich than its protonated counterpart, which suggests that it would be more rapidly oxidized by hydrogen peroxide, and this species is more abundant at pH levels higher than the first pK\textsubscript{a} of the Fe\textsuperscript{III}-TAML complex\textsuperscript{159}.

\textbf{1.5.10 Degradation of Fe-TAML catalyst}

There are two known major pathways for the degradation of Fe(H\textsubscript{2}O)\textsuperscript{B*(CH\textsubscript{2}CH\textsubscript{3})}\textsuperscript{+} complexes. One of these results in macrocyclic ring rupture and the formation of a hydantoin-containing product. The second involves acid induced demetallation of the complex. During catalysis, the TAML complexes slowly degrade. The primary degradation process is first initiated through a H-atom abstraction. Here, both an intermolecular and an intramolecular abstraction is possible, however it is likely that the intramolecular process will dominate when the catalyst concentration is low and substrate concentrations are high\textsuperscript{142}. This is illustrated in
Figure 44 using the H₄B⁺ analogue that contains two geminal ethyl groups. It is believed that the [FeB*(Cl)]²⁻ complex degrades via a similar pathway.

Figure 44: Mechanism for one degradation pathway of activated of Fe³⁺-TAML complexes

The second issue associated with these complexes is the buffer induced demetalation of the macrocycle. The cleavage of a single Fe-N bond leads to rapid hydrolysis of the remaining three Fe-N bonds. Brønsted acid components of a buffer solution can demetalate the complex (Figure 45). This usually happens between pH 4 and 9. For instance, demetalation can be induced by phosphate components.
Alternatively, phosphate induced demetalation may occur between pH 3 and 4. Fortunately, the rate of demetalation is significantly slower than that of oxidation. This property however prohibits long term storage of the complexes in buffered solutions\textsuperscript{166}.

1.5.11 Conclusion

In summary, the idea of green chemistry, and in particular the application of oxidation catalyst in water purification, was explored in this chapter. The use of a wide range of methods to remove EDCs and pharmaceuticals in wastewater has been greatly studied. The used of the effective bio-inspired catalysts known as Fe-TAMLs for oxidations with hydrogen peroxide in homogenous systems was summarised in the final part of the chapter.
CHAPTER 2
2.1 CHAPTER 2 SUMMARY

This chapter will be introduced with a brief overview of the target novel oxidation system, how it works and how it can be applied in practical situations. Next, the design and synthesis of the smart polymer film that is an essential component of the new oxidation system and its use in conjunction with specific catalysts will be discussed. In addition, the key features that this smart polymer oxidation system embodies and how this differs from standard commercial membranes and their application will be outlined.

Following the introduction to this chapter is an in depth discussion of the key porous polymer that was prepared using chloromethylstyrene as the starting material. This is followed by a description of the novel method that was developed to cast and cure the smart polymer film, how the polymer brushes were attached to it, how the catalyst was anchored to the base of the brushes and finally how the six best methods of preparation or the porous polymer films were selected. This involved a screening test that was based on the permeability of aqueous carbonate buffer solution and the effectiveness of bleaching of orange (II) dye once the catalyst had been added. More detailed investigations of the bleaching experiments are discussed in depth in chapter 3.
2.2 Description of the new oxidation system and how it works

The aim of designing the new oxidation system was to develop a process that would enable the purification of large volumes of water by the oxidative destruction of harmful minor contaminants such as pesticides, endocrine disruptor compounds and active pharmaceutical ingredients (i.e. compounds of emerging concern, CEC), without the introduction of excess oxidant, base or catalyst to the bulk solution. The oxidation system utilizes hydrogen peroxide in conjunction with the newly developed iron-based oxidation catalysts known as Fe-TAMLs®. Fe-TAMLs were specially designed to be water soluble and non-toxic and are known to be very active at sub-micromolar concentrations. They efficiently and rapidly catalyse oxidations by hydrogen peroxide and other peroxy compounds (Figure 46).

![Figure 46: Fe-TAML catalytic oxidation scheme](image)

Currently these are homogeneous catalysts and they are exclusively used in aqueous solutions with excess hydrogen peroxide. However this is not a viable approach for the above application because of the contamination of the bulk solution and the cost of using excess reagents and catalyst. The particular oxidation system that has been developed could find application and uptake world-wide, especially as it potentially provides a means to achieve cost-effective purification of drinking water, or the remediation of contaminated waste water streams.
2.2.1 Description of the technology

A novel multi-functional smart polymer film was developed to enable a simple purification process of this type to become a reality. A diagram that illustrates the principles behind the mode of action of the new oxidation system is given in Figure 47. The key component is the porous smart film or multi-functional membrane. This serves to keep the hydrogen peroxide oxidant solution (<4%) from mixing directly with the bulk water sample, it anchors the catalyst, concentrates the impurities to be oxidised and allows the slow perfusion of hydrogen peroxide/buffer solution to the catalyst centres so these can be activated and hence oxidise the concentrated impurities to harmless compounds. The rate of perfusion of the hydrogen peroxide/buffer solution is controlled by the pressure placed on the hydrogen peroxide solution. In laboratory experiments sufficient pressure is conveniently produced by arranging for the peroxide solution to have a small hydrostatic head, i.e. for the height of this solution to be above that of the substrate solution by about 10-30 cm. The positively charged quaternary ammonium groups that form part of the surface polymer “brushes” attract and hold fast the negatively charged oxidation catalyst molecules (e.g. [Fe-TAML]) by simple electrostatic and supramolecular interactions. The long alkyl chains form a relatively hydrophobic layer (i.e. a “carpet” or “brush” zone on the membrane surface that selectively attracts and concentrates organic pollutants are brought into direct contact with the oxidation catalyst molecules that are anchored at the bottom of the alkyl chains and are adjacent to the surface of the membrane. As the hydrogen peroxide perfuses through the membrane, it first encounters the catalyst molecules as it exits the membrane. In a very rapid reaction, it activates the catalyst molecules

Figure 47: Schematic diagram of the overall oxidation system that utilises Smart Catalytic Films (SCFs)
within the brush to form a highly reactive oxidising species. These reactive species very rapidly oxidise the nearby CECs to harmless products. The harmless oxidised products, which are much more hydrophilic in nature, then diffuse back into the bulk water. It should be noted that hydrogen peroxide alone (i.e. without the Fe-TAML catalyst present) does not oxidise most CECs at useful rates.

Key features of the specially functionalised membrane are (i) The perfusion rate of the hydrogen peroxide can be controlled by the pressure applied to the hydrogen peroxide solution. In this way the leakage of excess hydrogen peroxide into the bulk water solution can be prevented and the rate at which the catalyst molecules are activated can be controlled. (ii) The water soluble catalyst molecules are strongly anchored to the membrane and they do not leach into the bulk water solution. (iii) When the catalyst molecules do eventually degrade, they can simply be replaced by contacting the membrane surface with an aqueous solution of fresh catalyst, thereby regenerating the fully functional membrane. (iv) In principle the alkyl chains can be substituted with a range of functional groups to enhance the attraction and concentration of specific pollutants, possibly even pathogens. (v) In principle, catalysts other than Fe-TAML could be used with this type of functionalised membrane. (vi) The system can be “infinitely” scaled up through simple engineering techniques such as combining modular units and could therefore be used for both small and very large scale water purification applications. (vii) The overall cost should not be prohibitive. Related membranes are already used in water purification and desalination on massive scales. The cost of functionalising the membrane and adding the catalyst to the membrane should not add unreasonably to the overall cost.

In this chapter, the design and synthesis of the smart polymer film is discussed. The synthetic methods used to make the polymer for the film are presented as well as the casting method used. Functionalization of the film and attachment of the catalyst molecules to produce the smart catalytic film is then discussed. In order to determine the performance of the smart thin films produced, preliminary screening tests were carried out which involved investigating the permeability and catalytic bleaching performance of the SCFs. Result obtained were then evaluated in order to choose the best SCFs for more detailed studies. Preliminary result are discussed in section 2.10 but the more detailed studies are the subject of chapter 3.
2.3 Smart polymer film formation

This particular oxidation system is very unusual in the sense that it uses a membrane as an oxidant delivery device rather than as a filtration device. Therefore a brief summary of the different types of commercial membranes that are available, their features, typical applications with respect to water treatment and what technology is currently available in terms of anchoring polymer brushes onto solid supports is given before making comparisons with the smart polymer film oxidation system that is the focus of this work.

2.3.1 Different types of membrane technology

Membranes in general are defined as discrete, thin interfaces that moderate the permeation of chemical species they are in contact with. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for example containing holes or pores of finite dimensions or consisting of some form of layered structure.\textsuperscript{172} Membranes can be divided in general into two large groups, those that are symmetrical (isotropic) and those that are anisotropic. Within the symmetrical group, membranes can be subdivided into three classes, isotropic micro-porous membranes, isotropic nonporous dense membranes and isotropic electrically charged membranes. Conversely for the anisotropic group, membranes can also be subdivided into three more classes, Loeb-Sourirajan anisotropic membranes, thin-film composite anisotropic membranes and polymer matrix membranes (Figure 48).
2.3.1.1 Isotropic micro-porous membranes

This membrane has common features of a typical filter with a rigid, voided structure with randomly distributed, interconnected pores\textsuperscript{172}. However, the striking difference with conventional filters can be observed in the pore size of the filter where the diameter of these pores can range from 0.01-to 10 µm. Particles that are larger than the largest pore size cannot pass through the membrane. As a consequence, the separation using micro-porous membrane is based upon two factors, pore size and molecular size distribution. In general, only molecules that differ considerably in size can be separated effectively by micro-porous membranes\textsuperscript{172}.

2.3.1.2 Nonporous, Dense membranes

This membrane is developed from a dense film where the driving force used for the transportation of permeate can be concentration, electrical potential gradient or pressure. The separation of various components of a mixture is related directly to their relative transport rate.
within the membrane. This is determined by their diffusivity and solubility in the membrane material. Hence, membrane separation is effective even for similarly sized permeates if the solubility of the permeates differ considerably. These dense membranes are normally used for experiments involving pervaporation, reverse osmosis and gas separation.

2.3.1.3 Electrically charged membranes
Most electrically charged membranes are of the micro-porous type where the walls of the pores consist of permanent positively or negatively charged ions. A membrane fixed with positively charged ions is referred to as an anion-exchange membrane because it binds anions in the surrounding fluid and vice versa for negatively charged membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much lesser extent by the pore size. The separation is affected by the charge and concentration of the ions in solution. For instance, separation of divalent ions is more successful compared to monovalent ions and selectivity is inversely proportional to ionic strength of the solutions. Common application of electrically charged membranes can be seen in electrodialysis.

2.3.1.4 Anisotropic membranes
In principle, the rate of transportation of compound across a membrane is directly proportional to the membrane thickness. To be economically beneficial, high rates of transportation are needed which requires the membrane to be as thin as possible. Nevertheless, early development of membrane technologies especially in film fabrication constrains the production of mechanically strong, defect-free films to about a thickness of 20µm. However, a recent breakthrough was developed to produce anisotropic membranes that have extremely thin surface layers supported on a much thicker, porous substructure. The layers can either be formed separately or in single operation while for a composite membrane, the layers are formed using different types of polymers. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer with the substructure functioning as a mechanical support. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such membranes.
2.4 Backing material used as membrane film support

There are many different types of commercially available backing materials that have been developed to support membranes. However, for this particular research, two types of backing membrane was chosen: polypropylene (PP) non-woven 2471 nd backing and a polyester backing. These very porous backing materials were chosen because as flat sheets they have quite high mechanical strength and are essentially inert to the chemicals they are exposed to during synthesis of the smart membranes and the use of these in hydrogen peroxide. Furthermore, these backing materials also contribute to the production of high performance smart membranes due to a high degree of uniformity in terms of thickness, porosity and surface properties. Moreover, they exhibit very good fibre bonding which is essential in order to reduce membrane defects.\textsuperscript{173}

The use of backing support materials is very important to provide mechanical strength to the chloromethylstyrene (CMS) polymer created. Membranes synthesized without any backing support often deteriorate and become fragile on a larger scale due to their tendency to shrink during thermal cross-linking.\textsuperscript{174}
2.5 Nanofiltration (NF) membranes

Membrane technologies have been developed that use the cross-flow concept. This principle enables a continuous flow of solution to occur during processing. Typically the bulk solution flows over and parallel to the membrane surface and, because this system is pressurized, water is forced through the membrane. The turbulent flow over the surface minimizes accumulation of particular matter (Figure 49).

Crossflow- membrane separation technologies are used on several membrane types such as reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), and microfiltration (MF). All of these are based on pore size exclusively. Microfiltration membranes have pore sizes ranging from 0.01 to 1 µm which remove sub-micrometer suspended materials but not the dissolved materials. Ultrafiltration membranes on the other hand are classified based on a molecular weight cut-off (MWCO) which is defined as the maximum molecular weight of a dissolved compound that will pass through the membrane. These membranes typically have pore sizes between 0.010 and 1µm (Figure 50). Hence, they can eliminate organic materials (macromolecules) which are larger than the pore size and this exit in the concentrate stream.

Nanofiltration membranes have a MWCO of less than 1,000 Daltons and are considered as “loose” reverse osmosis membranes since they can reject dissolved ionic contaminants, but to
a lesser degree than reverse osmosis.\textsuperscript{176} NF membranes have the ability to reject multivalent salts to a greater extent than monovalent salts (for example, 99\% vs. 20\%). \textsuperscript{176}

The last types are reverse osmosis membranes where the best permeate results are obtained with respect to any pressure driven membrane technology used. This membrane has MWCO values between 50 to 100 Daltons and can reject up to 99\% of all ionic solids (Figure 51). The salt-rejection of NF and RO is not yet fully understood but some experts endorse a theory that pure water preferentially passes through the membrane while others attribute salt rejection to the effect of surface charge of the membrane polymer upon the polarity of the water\textsuperscript{176}. For this particular research, membranes of the NF type were used since these were considered to be the most suitable membrane for slow controlled perfusion of hydrogen peroxide/buffer solutions that are relevant to this research (Figure 52).

![Figure 50: Microfiltration retains the feed's suspended solids (left) and the UF separates macromolecules (right).](image)

![Figure 51: Reverse Osmosis membranes yield the cleanest permeate](image)
2.5.1 Transport and selectivity models for NF and low MWCO UF membranes

Typical aqueous applications of NF membranes include the separation of salts from dye solutions and the separation of acids from sugar solutions. Although NF membranes are readily available in the market, “tailor-made” membranes are still required to deal with various solute sizes, shapes, MWs and charges. Variations in the solute properties can also cause variability in rejection and this affects the permeability of the membranes. A fundamental analysis of membrane transport is therefore needed to understand the changes in the transport mechanism, especially when new types of polymers are used to produce NF membranes. For conventional NF membranes, three main solvent and solute transport mechanisms are thought to exist: Donnan exclusion, pore-flow and solution-diffusion.

Figure 52: The applicability ranges of different processes based on sizes
2.5.2 Advantages of membrane technology

Membrane technologies possess several advantages that make them very popular to use in separation processes such as those indicated below\textsuperscript{176}:

- Continuous processing, with automatic and uninterrupted operation.
- Low energy use involving neither phase nor temperature change.
- Modular –design, so that there are no significant size limitations
- Minimum number of moving parts, with low maintenance requirements
- No effect on form or chemistry of the contaminant.
- A discrete membrane barrier for physical separation of contaminants.
- Absence of chemical –addition requirement to effect the separation.

2.5.2.1 Advantages of using NF membranes\textsuperscript{172}

Nanofiltration membrane is the major type of interest in this project. This is because NF is the latest development in membrane technology where the pore size incorporates the lower end region of ultra-filtration and upper end region of reverse osmosis. This type of membrane is only applicable for dissolved materials and not suspended particles. This leads to the invention of thin-film composite (TFC) membranes which carry out high levels of separation at high fluxes. Moreover, these membranes have become widely used due to their versatile capabilities in several transport mechanisms such as simple diffusion, Donnan-exclusion and convection. NF membranes also have slightly open membrane morphology and higher surface charge density in comparison with dense RO membranes\textsuperscript{172}. This leads to lower separation efficiency particularly for monovalent ions. However, this NF membrane can still function at lower pressure to give the same flux.

The Nanofiltration concept is described based on cross-flow operation which is classified on the basis of the pore size of the membrane which in turn determines the size of molecules corresponding to the molecular weight cut off (MWCO) of approximately 200-1000 Dalton (Da), and operating pressures of 150-500 psi (10-34 bars)\textsuperscript{172}. For typical types of NF membrane, water permeability is on the order of $2 \times 10^{-4}$ cm$^3$cm$^{-2}$ bar\textsuperscript{177}. In addition, recent NF membranes nowadays have negatively charged groups such as carboxylic groups which will provide significant selectivity based on both size and charge\textsuperscript{177}. The primary purpose of NF
membrane is to separate mostly multivalent salts and organic compounds with low molecular weight. The first industrial systems using NF membranes were installed in 1978 using tubular membranes for desalination of dyes and brighteners\textsuperscript{172}. There are two common ways that could be used to produce NF membranes. The first method uses polysulfone and cellulose acetate as starting materials while the second method uses polymer phase inversion. Both result in production of a homogeneous asymmetric membrane\textsuperscript{172}. The separation occurs by diffusion of the molecules of the solvent through the mass of the membrane material (driven by high pressure differential), and not through any physical hole (or pore) in the membrane. Depending upon the purpose of the separation, some of the solute molecules may also diffuse\textsuperscript{172}. Most of all, the biggest advantages using membrane processes is due to their lower emissions to the environment, relatively low energy consumption and better product quality which can provide lucrative alternatives to traditional unit operations\textsuperscript{177}.

### 2.5.3 Factors affecting the performance of NF membranes

**Pressure**: Pressure differences are the driving force responsible for a NF process. The effective driving pressure is the applied hydraulic pressure minus the osmotic pressure applied on the membrane by the solutes.

**Temperature**: The flux of the solution across the NF membrane is directly proportional to the process temperature due to viscosity reduction. However, the rejection properties of NF membranes are not significantly dependent on the process membrane.

**Cross-flow velocity**: Increasing the cross-flow velocity in an NF membrane filtration process increases the average flux due to efficient removal of the fouling layer from the membrane surface. Nevertheless, factors such as the type of element used, system hardware as well as mechanical strength of the membrane significantly dictates the degree of cross-flow velocity. Using NF membrane at very high cross-flow velocity can lead to premature failure of membranes and modules.

**pH**: pH can affect performance of NF membrane in several ways. For example, the negatively charged sites on NF membranes, which are normally maintained at neutral or basic pH, can be altered significantly at lower, acidic pH. Even though it is widely established that typical RO and NF membranes have lower rejection at low pH, the fact that different suppliers of the membranes use different chemistry to produce the thin layer of the membrane should be taken into consideration. The pH dependency of a membrane should be determined for each membrane type prior to use. Moreover, pH also effects the membrane performance which can
be demonstrated with the example where the change of solubility of ions at different pH regimes, which cause different rejection rates.

**Salinity:** The effective pore radius of a charged pore will increase as the ionic strength of the surrounding liquid increases. Therefore, the rejection of monovalent ions will decrease as their concentration in the feed solution increase. The rejection of divalent ions will be affected to a lower extent.

Molecules may also diffuse. Most of all, the biggest advantages using membrane processes is due to their lower emissions to the environment, low energy consumption and better product quality which can provide lucrative alternatives to traditional unit operations.

### 2.5.4 Applications of NF membranes

Several recent studies have showed the wide applications of NF membranes to solve different problems such as:

#### 2.5.4.1 Use in polishing of conventional water treatment and wastewater treatment systems

NF membrane technologies have proved to be successful methods to remove dissolved low molecular weight organic and coloured compounds from secondary effluent of biologically treated effluent. When an NF membrane system was established to treat effluent from a paper mill, it was found it could remove between (80-90)% of the hardness, carbon oxygen demand (COD) and sulfates. Another application was observed in the US to treat river water which was used as a water supply source. The conventional method for water treatment was not applicable due to significant seasonal fluctuations in total dissolved solids, and the effluent from the water treatment facility did not always supply water at the desired quality. Hence, using NF membrane technologies was the best solution because it not only overcame fluctuations in supplying high quality water but was also the most efficient, reliable and economical method for the application.

#### 2.5.4.2 Softening of seawater and brine solutions

Seawater is used as the main source of NaCl for production of soda ash. However, seawater has other components such as sulfates that need to be removed prior to use. It was discovered that NF membrane technologies are the most effective and efficient method of removing sulfates, mostly by negatively charged NF membranes, in the 200 MWCO range. Another application is in the oil and gas industries. Seawater is often injected into offshore oil wells to displace the oil. Due to the high sulfate content in the seawater and the high barium and
strontium content in the wells, there is potential for significant scaling and possible reservoir souring. These scale deposits are a common problem. Conventional treatment of this problem required the use of high doses of antiscalants which is labour intensive, economically inefficient, technically difficult to control and environmentally unfriendly. In the late 1970s, a membrane solution was introduced; which involved the use of NF membranes to remove the sulfate from the seawater before injection. The volumetric recovery of the process was between 75% and 80%. The concentrate stream is returned to the sea.

2.5.4.3 Dairies and –whey treatment

NF membranes are widely used in the dairy industry to treat whey, a protein by-product of cheese making. Typically, whey is first treated with UF membranes, to concentrate the protein to a usable level. The UF permeate, containing lactose and salts is then processed with NF or RO to concentrate and demineralise the lactose solution. NF is often used in the last stage of an RO system in dairy processing, to minimize osmotic pressure and allow concentration to the desired level. In this case, permeate from the NF stage is recycled back, so that permeate quality is not compromised.

2.5.4.4 Food Industry

In this industry, NF membranes were used with respect to gelatine concentration. Conventional ways to produce gelatine gave product ranging from medium to high concentration. Using UF membranes provides major drawbacks during the processes such as high losses, particularly when low bloom gelatin is produced. Nevertheless, by using NF membranes, which can operate at moderate to high-temperatures, allowed gelatine manufacturers to use them effectively, with minimal to non-detectable losses.

2.5.5 Negatives features of using membrane filtration

Although membrane filtration, especially using reverse osmosis membranes, can be used to purify water, this particular process suffers from a number drawbacks when used on very large scales. These include the cost of replacing the membranes, fouling, and the high energy consumption required for their use. Membranes with larger pores such as NF membranes are not able to remove most dissolved organic pollutants. It is anticipated that the SCFs will not suffer from these same problems.
2.6 General principles of the smart thin film can be summarized as below:

- Functionalize the membrane to add long chain hydrocarbon brush components
- Must be porous for hydrogen peroxide delivery
- Need to have sites to anchor catalyst (either + or – charge)
- Concentrate pollutant in brushes and bring close to catalyst site for oxidation.
- The polymer chosen for membrane formation and functionalization was polychloromethylstyrene

2.7 Traditional method to prepare Chloromethylstyrene polymer

The initial aim of this project was to develop a membrane polymer that could be functionalized with the appropriate brushes. Since no commercial starting polymer membrane of this type was available, a membrane polymer derived from the polymerization of chloromethylstyrene (CMS) was developed. CMS was chosen because the ability of chloromethyl groups to undergo reactions with a wide range of reactants to form new derivatives. By starting with CMS, many of the problems, costs and hazards associated with chloromethylating styrene itself can be eliminated\textsuperscript{179}.

In the past few decades, chloromethylstyrene polymers (CMSPs) have been made on a large scale. However, because of the specific characteristics of the polymers and the applications that our system needs to exhibit, some modifications of reported procedures were used. These are discussed below.

The synthesis of CMS/styrene block copolymers using controlled radical polymerization was studied by Denis and Bernard. Bulk polymerization of styrene or chloromethylstyrene was performed using benzoyl peroxide (BPO) as the initiator in the presence of 2, 2, 6, 6-tetramethyl-l-piperidinyloxy (Tempo). Polymerizations were carried out with distilled monomers, under a nitrogen flow and vigorous stirring. The distillation presumably removed the stabilizer, tert-butyl catechol (TBC), although this was not specifically noted. By using this technique, Mn values can be obtained less than or equal to 1.5 and block copolymer PCMS-b-PS formed (12,000/60,000) with and PCMS-Tempo macro initiator efficiency closed to 85 $%$\textsuperscript{180}. 
Others have also tried studied copolymerization of chloromethylstyrene and styrene using free radical polymerization techniques. In this literature, co-polymerizations of p-chloromethylstyrene with styrene and methyl methacrylate were carried out in a sealed tube at 60°C. The required amounts of p-chloromethylstyrene, co-monomer, AIBN, and benzene as solvent were charged into a Pyrex glass tube, which was then degassed under vacuum by the conventional freeze, pump, thaw technique and sealed off under vacuum. All copolymerizations were carried out with shaking under 10% conversion.

After copolymerization for a given time the tube was opened and its contents were poured into a large amount of methanol to precipitate the copolymer. The resulting copolymers were then purified by reprecipitation of a benzene solution with excess methanol. The composition of the copolymers was calculated from their elementary analysis of chlorine. The monomer reactivity ratios ($r_1$ and $r_2$) were obtained by the Fineman-Ross method. The TBC stabilizer was not removed in this method$^{181}$.

Others have also tried to synthesis and functionalize reactive monodisperse macroporous poly(chloromethylstyrene-co-styrene-codivinylbenzene) beads by a staged template suspension polymerization. This synthesis can be divided into a two stage process where the first stage is to prepare porogen particles followed by the preparation of porous beads.

An earlier method also focused on the preparation of the CMS polymer using emulsion techniques using monodisperse polystyrene template particles 930 nm diameter, 9.1% solid in 0.25 wt% aqueous sodium dodecyl sulfate (SDS) solution, (1.06 mL), prepared activated by adsorption of an emulsion of 0.96 mL$^{-1}$ chlorodecane in 25 mL of 0.25 wt% aqueous SDS solution. The swelling was allowed to proceed at room temperature for 4h.

An emulsified mixture containing varying amounts of styrene and benzoyl peroxide (BPO) was added to the dispersion resulting from the previous step, and the swelling was continued for another 5h. Sodium nitrite was added to achieve a total concentration of 0.013 g/mL. A sufficient amount of 5% wt/vol aqueous poly vinyl alcohol solution (Mw 85,000-146,000, 87-89% hydrolyzed) was added to the dispersion of swollen particles to adjust the total concentration of polyvinyl alcohol to 1% (wt/vol). The mixture was deaerated by purging with nitrogen for 20 min in a 250 mL glass reactor (Buchi BEP 280). The reactor was sealed, and the polymerization was carried out at 70°C for 24 hours. The resulting uniform beads of linear polystyrene thus formed served as the polymeric porogen in the next reaction step and were used without further purification$^{182}$. 
Others have also reported the formation of a polystyrene polymer on beads to use as sensors for pH. Polymerization was carried out by adding 50 mL of the solution of monomer, crosslinker and additives to 500 mL of water containing 0.040 g of xanthan gum and 0.028 g of hydroxybutyl methyl cellulose to complete the reaction. In all experiments, 1.5% benzoyl peroxide was included in the organic solution to initiate free radical polymerization. The mixture was stirred at 180 rpm for seven hours at 85°C. After the polymerization was complete, the beads were removed by filtration, washed with acetone and dried in air.

Amination was carried out by adding 20 mL of anhydrous diethanolamine to a flask containing poly(vinylbenzylchloride) beads. Usually, the polymer beads were preswollen in dioxane to shorten the rate of the amination reaction. The mixture was kept at room temperature for two days with intermittent shaking. Then, the product was treated with a dilute solution of acid three times followed by deionized water. The beads were then dried in the fumehood overnight.

In conclusion, the standard methods employed to synthesize chloromethylstyrene polymers is through either radical, suspension or emulsion polymerisation techniques. Attempts were also carried out to make copolymers of styrene and CMS using radical initiators such as BPO or AIBN. Most of the reported polymerization methods were carried out without removing the inhibitor tert-butyl catechol and were normally carry out using beads as a solid support.

### 2.8 Different synthetic methods used to make polychloromethylstyrene

**Method A**

After considering the different literature procedures to make polychloromethylstyrene, the method below was initially chosen since it was simple and would form a porous membrane film with the required characteristics. The method chosen involved the use of CMS, divinylbenzene (DVB), Kraton (G6932/G6945), the radical initiator benzoyl peroxide (BPO), in a solvent mixture of xylene and dodecane. This solution was stirred and heated in an oil bath at 85°C until it had the appearance of maple syrup or liquid honey (i.e. the viscosity reached approximately 600-800 centipoise at 25 °C).

In the initial experiments, Kraton was added as a toughening agent. Kraton is a triblock copolymer of styrene-ethylene-butylene and was added to further enhance the physical
properties of the polymer formed. Unfortunately, the same grade of Kraton that was used in literature preparation (G1652) could not be sourced, hence trials were carried out using Kraton, G6945 or G6932 which have similar characteristics to the Kraton used in the reported preparation. Using these two Kraton materials percentage of Kraton was varied between 2% and 6% in small scale experiments. It was observed that the more Kraton that was added, the more quickly the solutions became viscous and they also became yellow in colour and cloudy. On the basis of these results, Kraton was subsequently not added to the reaction mixtures and this omission did not adversely affect the properties of the polymers formed.

Apart from varying the percentage of Kraton, the percentage of free radical initiator, BPO was also varied. The percentages of BPO added were increased from 0.5% - 2.0% to minimize the time taken to form the viscous solution. However, one drawback was that, if more radical initiator was used, the polymer chains formed were much shorter (as found by GPC analysis). Slight changes were made by changing n-decane with dodecane but no changes can be observed on the final polymer.

In addition, preliminary tests were also done using azobisisobutyronitrile (AIBN) as the free radical initiator instead of BPO. This was done because in the polymer industry AIBN is one of the more common ways used to initiate radical polymerization as it is easier to control the polymerisation compared to using BPO. Experiments with AIBN were carried out under normal conditions in conical flasks in the presence of oxygen (with cotton wool plugging the flasks) as well as in a schlenk tube under nitrogen gas. Examples of this radically initiated polymer synthesis being carried out either in air or under an inert gas have been reported.

**Method B**

Another polymerisation method that was explored involved the addition to the reaction mixture of chloromethystyrene (CMS) with the inhibitor (TBC) still present. The mixture was stirred under N₂ in an oil bath at 80-85°C for (50 hours). During this time the solution did not become as viscous as expected. On the 6th day the solution was poured into excess n-hexane and the solid formed removed by filtration. The mass of the polymer obtained was only 158.4 mg. This very small amount indicates that a polymer with short polymer chains was formed.
Method C

In another synthetic procedure the inhibitor, tert-butyl catechol (TBC), was removed from the CMS by shaking with 0.5% aqueous NaOH before polymerisation reactions were carried out. In preliminary experiments pure CMS, xylene, dodecane, DVB and AIBN were mixed and stirred under nitrogen in an oil bath at (80-85) °C.

Method D (preferred)

In this procedure the polymerisation of CMS was carried out without the addition of diluting solvents, i.e. neat CMS was polymerised. This is often referred to as homopolymerization. In this method, a schlenk tube was charged with pure CMS (inhibitor removed) and heated in an oil bath at 85°C under vacuum until a viscous liquid was obtained. This usually occurred after several days. Any remaining monomer was removed by dissolving the viscous liquid in methyl ethyl ketone MEK (5%) and then adding this solution to methanol to cause precipitation of the polymer as white flakes.

Method E

An emulsion method of polymerisation was also investigated. The following procedure was used in order to prepare high molecular weight linear and lightly cross-linked polymers of CMS. In this method CMS (TBC not removed), methyl acrylate, varying percentages of DVB (0.00, 0.05, 0.3 and 1.0% w/w), deionized water, 20% sodium lauryl sulfate (V/V), 5% NaHCO₃ and K₂S₂O₃ were added to a clean bottle. This mixture was then cooled in an ice bath for one hour before an aqueous solution of Na₂S₂O₅ (5% V/V) was added. The bottle was purged with nitrogen for 20 minutes in an ice bath before it was sealed with parafilm. The bottle was slowly stirred at 30-50 rpm at 25°C for a few days. The viscosity of the resulting solution was very low and so the normal casting procedure was not able to be used. Instead the polymer was “painted” onto a substrate using a brush.

Method F (preferred)

To see if the nature of the monomers influenced the polymerisation process and the properties of the resulting polymer, experiments involving the co-polymerization of styrene and CMS (1:1) were also investigated. This was done by first removing the inhibitor in both styrene and in CMS by shaking with 2.5% and 0.5% NaOH (w/v) aqueous NaOH solutions, respectively. This was followed by washing the monomer solutions with deionized water until the water was
neutral. The styrene and CMS were then added together with DVB, dodecane, xylene and AIBN and heated in an oil bath at 85°C with stirring speed 150 rpm, as per the procedure outlined in Method B above. Copolymerisation of styrene and CMS was also investigated using the neat monomers without added solvent (as per Method D above).

After evaluating the polymers formed in all of the polymerisation experiments carried out under the general procedures outlined in the Methods A-F above, six of the best polymer synthesis methods were selected based on the permeability of the membranes formed from the polymers and also the bleaching performance of the polymer membranes after functionalization and addition of catalyst. Details of these basic performance tests are discussed below in section 2.10. The polymerisation methods selected for further study are given in Table 9 below:

<table>
<thead>
<tr>
<th>Polymer Number</th>
<th>Polymerisation procedure</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCMS + solvent (DVB+ AIBN+ xylene+ dodecane)</td>
<td>C</td>
</tr>
<tr>
<td>2</td>
<td>PCMS + 0.5% DVB + NMP</td>
<td>D</td>
</tr>
<tr>
<td>3</td>
<td>Copolymer + DVB 0.5% + NMP</td>
<td>F</td>
</tr>
<tr>
<td>4</td>
<td>Copolymer + NMP</td>
<td>F</td>
</tr>
<tr>
<td>5</td>
<td>Emulsion polymer</td>
<td>E</td>
</tr>
<tr>
<td>6</td>
<td>PCMS + NMP</td>
<td>D</td>
</tr>
</tbody>
</table>

Table 9: Different type of polymerisation procedures

In Figures 53–55 the 3 basic polymerisation processes using methods D, E and F, which correspond to homopolymerization, emulsion and copolymerisation of styrene and CMS, are illustrated.
2.8.1 Homopolymerization of Chloromethylstyrene

Figure 53: Homopolymerization of Chloromethylstyrene

2.8.2 Copolymerization of 50% styrene, 50% chloromethylstyrene

Figure 54: Copolymerization of styrene: chloromethylstyrene (1:1) mole ratio

2.8.3 Emulsion polymerization of CMS

Figure 55: Emulsion polymerization of CMS
2.8.4 Images of PCMS formed by the solventless method

Figure 56: Thick layer of polymer after curing on a glass slide with pinholes

Figure 57: Early experimental results using method A with Kraton G6932 on (left flask) and Kraton G6945 on (right flask)
Figure 58: LHS images of CMS washed with 0.5% NaOH, followed by deionized water wash in the middle and lastly CMS treated with K$_2$CO$_3$ (anhydrous) to remove remaining traces of water RHS.

Figure 59: Solvent method with inhibitor TBC being removed and heated in oil bath at 85°C for 5 hours under N$_2$ atmosphere. LHS images of CMS washed with 0.5% NaOH, followed by deionized water wash in the middle and lastly CMS treated with K$_2$CO$_3$ (anhydrous) to remove remaining traces of water RHS.
2.8.5 Images during emulsion polymerization

Figure 60: Image 1 shows the solution containing deionised water, sodium lauryl sulfate, sodium hydrogen carbonate and potassium persulfate, image 2 after addition of CMS, methyl acrylate and DVB, image 3 shows the emulsion polymer cooling in ice bath and finally image 4 shows the emulsion polymer after stirring for 5 hours.
2.8.6 Images during Copolymerization reaction

Figure 61: Image 1 shows the mixture of CMS and styrene (1:1) mole ratio before heating, image 2 shows the viscous polymer formed, image 3 shows the addition of MEK while image 4 shows the formation of white flakes of polymer after precipitation.
2.8.7 Gel Permeation Chromatography GPC

To determine the average chain length of the polymer formed, gel permeation chromatography (GPC) was used. GPC is a type of size exclusion chromatography (SEC) that separates analytes on the basis of size\textsuperscript{186}. The most important parameters when characterizing polymers is the polydispersity index (PDI) which is defined as the distribution of polymer chains with particular molecular weights. Polymers can be characterized by a variety of definitions for the molecular weight including the number average molecular weight (M\textsubscript{n}) which is defined as the number of molecules per unit mass (average chain length), the weight average molecular weight (M\textsubscript{w}) is defined as the average molecular mass in the sample. GPC allows for the determination of PDI as well as M\textsubscript{v} and based on other data, the M\textsubscript{n}, M\textsubscript{w} and M\textsubscript{z} can be determined.

2.8.7.1 How GPC work in general

Separation occurs based on the size or hydrodynamic volume of the analytes. This differs from other separation techniques which depend upon chemical or physical interactions to separate the analytes. Separation occurs via the use of porous beads packed in a column.

2.8.7.2 Schematic of pore vs. analyte size

The smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. Conversely, larger analytes spend little if any time in the pores and are eluted quickly. All columns have a range of molecular weights that can be separated.

![Figure 62: Schematic representation of Molecular weight vs elution volume](image)

If an analyte is either too large or too small it will either be not retained or it will be completely retained respectively. Analytes that are not retained are eluted with the free volume outside of the particles (V\textsubscript{o}), while analytes that are completely retained are eluted with volume of solvent...
held in the pores ($V_i$). The total volume can be considered by the following equation, where $V_g$ is the volume of the polymer gel and $V_t$ is the total volume:

$$V_t = V_g + V_i + V_o$$

As can be inferred, there is a limited range of molecular weights that can be separated by each column and therefore the size of the pores for the packing should be chosen according to the range of the molecular weight of the analyte to be separated. For polymer separations the pore sizes should be on the order of the polymers being analysed. If a sample has a broad molecular weight range it may be necessary to use several GPC columns in tandem with one another to fully resolve the sample.

### 2.8.7.3 Summary of GPC results obtained

The samples were analysed before the polymer was cast onto the backing and functionalized and the results are tabulated in Tables 10 - 12. Batch numbers 1-5 in table 10 represent polymer PCMS made using same homopolymerization method (see section 2.8.1) but prepared at different times. Batches 1-3 in Table 11 represent polymer made using the solvent method (see section 2.8.1) without removal of TBC. This was done either by the polymer itself or with addition of 0.5% kraton or 0.5% BPO. Batches 1-3 in Table 12 represent copolymerization of 50% styrene and 50% CMS prepared using same copolymerization method (see section 2.8.1) with variations such as addition of 0.5% DVB but prepared at different times.

#### 2.8.7.3.1 PCMS only and/PCMS +0.5% DVB after TBC (initiator) being removed

<table>
<thead>
<tr>
<th>Batch</th>
<th>Concentration of polymer in toluene (mg/mL)</th>
<th>Sample type (all polymerised with no solvent)</th>
<th>$M_w$ (Da)</th>
<th>$M_n$ (Da)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.20</td>
<td>PCMS batch 1</td>
<td>213 000</td>
<td>140,000</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>3.40</td>
<td>PCMS batch 2</td>
<td>533 000</td>
<td>134,000</td>
<td>3.98</td>
</tr>
<tr>
<td>3</td>
<td>4.60</td>
<td>PCMS batch 3</td>
<td>545 000</td>
<td>305,000</td>
<td>1.79</td>
</tr>
<tr>
<td>4</td>
<td>4.67</td>
<td>PCMS batch 4</td>
<td>318 000</td>
<td>199,000</td>
<td>1.60</td>
</tr>
<tr>
<td>5</td>
<td>4.30</td>
<td>PCMS batch 5</td>
<td>872 000</td>
<td>376,000</td>
<td>2.32</td>
</tr>
<tr>
<td>6</td>
<td>2.73</td>
<td>PCMS+0.5% DVB batch 1</td>
<td>374 000</td>
<td>78,000</td>
<td>4.81</td>
</tr>
<tr>
<td>7</td>
<td>2.80</td>
<td>PCMS+0.5% DVB batch 2</td>
<td>889 000</td>
<td>248,000</td>
<td>3.59</td>
</tr>
</tbody>
</table>

Table 10: Summarized GPC results for PCMS only and/PCMS +0.5% DVB after the TBC was removed
This result shows that the Mw using solventless method range from approximately 213 000-872 000 with respective range of PDI index coming between 1.53-3.98. As might expected the solventless method of polymerisation with addition of 0.5% of cross linking agent DVB gave a higher Mw range from 374 000-889 000 with a larger PDI index range between 3.59-4.81. Despite having quite a big range of Mw from batch to batch using the same polymerization method, no significant differences in performance of the finished smart film were observed, presumably because the cross-linking step produced very similar insoluble, polymeric products. (dn/dv) corresponds to the refractive index in a specific solvent (toluene) that was obtained from literature values 0.192187. The Mw measurements recorded here are the values obtained before the polymer was cured and functionalised. It is noteworthy that attempts to dissolve the polymer samples after they had been cured and cross-linked were not successful. This indicates that the cross-linking procedure was successful and that a totally insoluble polymeric material was obtained.

2.8.7.3.2 PCMS solvent method (TBC not removed)

<table>
<thead>
<tr>
<th>Batch</th>
<th>Concentration (mg/mL)</th>
<th>Sample types</th>
<th>Mw (Da)</th>
<th>Mn (Da)</th>
<th>PDI(Mw/Mn)/</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.85</td>
<td>PCMS solvent + 0.5% Kraton</td>
<td>17,000</td>
<td>6,000</td>
<td>2.87</td>
</tr>
<tr>
<td>2</td>
<td>4.15</td>
<td>PCMS solvent</td>
<td>40,000</td>
<td>20,000</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>3.53</td>
<td>PCMS solvent + 0.5% BPO</td>
<td>35,000</td>
<td>20,000</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Table 11: Summary of GPC results for PCMS only or with 0.5% Kraton or 0.5% BPO using solvent method without TBC being removed

These results show that if the TBC was not removed prior to polymerisation, much shorter polymer chains were formed. These ranged from Mw 17,000- 35,000 with PDI value range from 1.76-2.87. Thus removal of the TBC is an important factor in ensuring that long polymer chains are obtained.
2.8.7.3.3 Copolymerization PCMS solvent method and/ Copolymerization PCMS + 0.5% DVB

<table>
<thead>
<tr>
<th>Batch</th>
<th>Concentration (mg/mL)</th>
<th>Sample types</th>
<th>Mw (Da)</th>
<th>Mn (Da)</th>
<th>PDI(Mw/Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.30</td>
<td>Copolymer batch 1</td>
<td>889,000</td>
<td>564,000</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>6.27</td>
<td>Copolymer batch 2</td>
<td>889,000</td>
<td>248,000</td>
<td>3.60</td>
</tr>
<tr>
<td>3</td>
<td>4.00</td>
<td>Copolymer + 0.5% DVB batch 1</td>
<td>403,000</td>
<td>150,000</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Table 12: Summary of GPC results for Copolymerization PCMS only or with 0.5% BPO using solvent method with TBC being removed

These results show that copolymerization of CMS/Styrene (1:1 ratio) with TBC removed gave polymers with Mw of approximately 889,000 and PDI values range from = 3.6-1.60. Copolymerization of CMS/Styrene (1:1) ratio with TBC being removed with addition of 0.5% DVB give Mw of approximately 403 000 and PDI values of 2.7. The most important parameter for the polymers synthesised for the smart catalytic films in this work is the Mw which is defined as the sum of the products of the molecular weight of each fraction multiplied by its weight fraction\(^\text{188}\). High average molecular weight values are crucial for this system to work as intended without slow dissolution or loss of polymer during operation and this has been successfully achieved. Since the polymer was prepared using a radical initiator (either BPO or AIBN), it may have had a very broad distribution of chain lengths \(^\text{189}\). This can be quantified using PDI values which corresponds to the breadth of the molecular weight distribution\(^\text{188}\). The PDI values overall ranged from 1.53-4.80 which shows that the different syntheses gave products with different distributions of polymer chain molecular weights. At this stage, these values can only be a point of reference since it is not certain whether larger or smaller PDI values are the most useful for this system. Indeed the PDI of the polymer may not be important since the polymer chains undergo a cross-linking procedure during the formation of the smart film. Overall the results show that it is hard to control Mw and PDI values in these radical polymerization reactions under the condition used.
2.8.8 Examples of the construction of porous CMS (or other polymers) films on backing materials.

Once the polymer was formed, the next step was to cast the polymer on a backing material in such a way that is made a porous film. This was achieved by following a literature procedure. 175

A number of different methods have been reported to make porous films from PCMS or polystyrene, but most involve casting the film with a porogenic solvent (or oligomer) present in the polymer, and then curing the polymer and removing the porogenic solvent. For example in one case CMS was mixed with DVB (2 mol %) and Kraton (2 % w/w), and in addition a 2:1 ratio of xylene:dodecane (40% v/v) was added as the porogenic solvents. After addition of the initiator (benzoyl peroxide) the CMS was polymerised to give a viscous partially polymerized material 190. This material was then spread between two 1” x 3” glass microscope slides separated by a spacer and cured by heating at 85°C for 6 h. After the porogenic solvents and unreacted monomer and crosslinker were removed by soaking in acetone for several hours, decanting, and then repeating the cycle.

A significant amount of work has been carried out previously to try and make microporous membranes as polymer electrolytes191. One recent examples is the preparation of a poly(vinylidene fluoride-co-hexa fluoropropylene) (PVdF-co-HFP) polymer film. This composite micro-porous membrane was prepared by dissolving PVdF-co-HFP and nano sized ZrO\textsubscript{2} in DMF. This was followed by the addition of PVA at different concentrations (0, 5, 10, 15 and 20 wt) % to give a viscous solution which was then spread as a film on the glass substrates using a doctor blade. The resultant nanocomposite polymer films were dried at 80°C in a vacuum oven for 6 h to remove any further traces of DMF. The cast nanocomposite polymer films were then immersed in a pool of deionized water at 60°C to dissolve the PVA and to obtain the micro-porous structure191.

Others have also shown that porous membrane films can be formed using the emulsion polymerization of styrene/DVB. For example, high internal phase emulsions (HIPEs) incorporating styrene, 4-vinylbenzyl chloride, divinylbenzene and ethylhexyl acrylate were used to prepare reactive, cross-linked porous membranes with an open cellular architecture and thicknesses between 30 and 500 µm. This was done by preparing a concentrated emulsion containing 75–85 vol% of the aqueous phase, sorbitan monooleate as a surfactant and 1 to 5 mol% of divinylbenzene in the oil phase, before casting on a polished glass substrate using a
casting blade. The spread of the emulsion was carefully covered with another glass plate and heated to 60°C for 24 h. The thickness of the resulting membrane depended on the thickness of the layer determined by the opening on the casting blade\textsuperscript{192}. The polymerised films had very few pinholes. In this work the solid polymer material we obtained from the polymerisation reactions was dissolved in the solvent NMP to give a viscous solution that had the right viscosity for casting in a thin film with a doctor blade. After casting, the polymer film was cured by heating and then soaked in n-hexane to remove residual solvent.

An essential part of this process was ensure the viscosity of the polymer solution was suitable for casting. To measure the viscosity of the polymer solution a rheometer was used. A short overview of rheometry and results obtained are summarized below:

**2.8.9 Rheometer techniques to measure viscosity**

A rheometer is an instrument that is used to measure the way in which a liquid, suspension or slurry flows in response to applied forces. It is used for those fluids which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer.

Viscosity is best determined using geometries in which the shear rate can be calculated from the dimensions of the measuring system and experimental data, such as the velocity or volumetric flow rate of a fluid or the rotational speed of a rotating cylinder, cone or plate\textsuperscript{193}. To understand the results obtained using a rheometer, one has to understand the different parameters measured and the units used in rheological measurements. Shear rate, denoted by the symbol \( \dot{\gamma} \), is the velocity gradient established in a fluid as a result of an applied shear stress. It is expressed in units of reciprocal seconds, s\(^{-1}\).

Shear stress is the stress component applied tangentially and commonly recognised with symbol sigma (\( \sigma \)). It is equal to the force vector (a vector has both magnitude and direction) divided by the area of application and is expressed in units of force per unit area (Pa).

Viscosity is the internal friction of a fluid or its tendency to resist flow. It is denoted by the symbol, \( \eta \) for Newtonian fluids, whose viscosity does not depend on the shear rate, and for non-Newtonian fluids to indicate shear rate dependency by \( \eta_a \). Depending on the flow system and the choice of the shear rate and shear stress, there are several equations to calculate viscosity. Here, it is defined by Equation 22 below:\textsuperscript{193}
2.8.9.1 Viscosity result batch 1 polymer

\[ \eta_a = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\sigma}{\dot{\gamma}} \]

Equation 22: Viscosity equation

Figure 63: Plot of Shear rate against shear stress for 4 different polymers
2.8.9.2 Viscosity result batch 2 polymers

Throughout this experiment, it was discovered that the viscosity was not that consistent for all of the polymers. The PCMS viscosity ranges from 0.0351 Pa.s to 0.165 Pa.s while the viscosity of Copolymer +0.5% DVB and PCMS + 0.5% DVB ranges from 0.0503-0.0539 Pa.s and 0.0778-0.106 Pa.s from batch to batch. However, for the polymer that being focussed on, no significant variation observed that could interfere with our end product.

From the representative data presented in Figures 63-64 it can be seen that the viscosity of the polymer solutions varied considerably between the different methods of polymer synthesis. PCMS materials synthesised give viscosity ranged from 0.0249 Pa.s to 0.080 Pa.s between batches while the viscosity of copolymers that contained +0.5% DVB ranged from 0.0503-0.0539 Pa.s and finally viscosity for PCSM + 0.5% DVB ranged from 0.0778-0.106 Pa.s from batch to batch. These values are far higher than monodisperse PCMS (Mw = 57,000) which is 0.0018 Pa.s\textsuperscript{194,195} which probably due to high branching shown by high PDI values and also due to high Mw (weight average molecular weight).
2.8.10 Casting techniques
Once the polymer had been synthesised and it was confirmed that the viscosity was in the correct range so that reasonable consistency was ensured between different batches, the polymer was cast onto the backing material. There are a number of different ways this can be done and these are briefly discussed below.

2.8.10.1 Dip coating
This is considered the most versatile method for liquid film deposition of a variety of inorganic and hybrid coating materials\textsuperscript{196}. This method is commonly used due to the simplicity of processing and handling, low cost and high coating quality\textsuperscript{197}. In addition, dip coating is also one of the few methods that allows a simultaneous double-sided coating of flat substrates which can be an advantage in some circumstances, e.g. in the production of optical filters. Typically, such films can be deposited with a single layer thickness ranging from only a few nanometers to approximately 200 nm for oxide coatings prepared from solutions of metal salts. Thicker films up to 1 μm thickness can be obtained from colloidal systems and even several microns are accessible with inorganic-organic hybrid materials, due to the lower shrinkage and the higher flexibility of these networks. In principle dip coating involved deposition of a wet liquid film by withdrawal of a substrate from a liquid coating medium. The overall process is depicted below in Figure 65:

Figure 65: Fundamental stages of sol-gel dip coating (the finer arrows indicate the flow of air)
Dip coating designates the deposition of a wet liquid film by withdrawal of a substrate from a liquid coating medium. The process of film formation in total implies several technical stages as demonstrated in Figure 65 but the underlying chemical and physical processes are mostly overlapping. This process starts with immersion of the substrates, a coherent liquid film is entrained on withdrawal of the substrate from the coating liquid, which then consolidates by drying and accompanying chemical reactions. To complete the final coating process, a further curing or sintering step (post-treatment) is then necessary.

2.8.10.2 Spin Coating techniques

This is a technique used for rapidly depositing thin coatings onto relatively flat substrates. The substrate to be covered is held by some rotatable fixture (often using vacuum to clamp the substrate in place) and the coating solution is dispensed onto the surface. The action of spinning causes the solution to spread out and leave behind a very uniform coating of the chosen material on the surface of the substrate. Despite being considered as an easy method to produce uniform surfaces, several defects can still occur which cannot be ignored. Examples of some known defects are striation defects, gradual radical thickness variation, Chuck Marks, and Comets. Thus to use this techniques one must have good understanding of how the solvent evaporates and the drying characteristic of the film.

Typical coating thickness values are usually below 1 micron when sol-gel films are deposited by spin coating. This is partly due to the relatively low solids loading that sol-gel solutions usually provide and the large amount of physical shrinkage that must accompany drying and film solidification. Attempts to make thicker coatings can result in profusely cracked coatings.

2.8.10.3 Flat spray process for optical coatings on cold glass

The thickness of optical coatings lies in the range of 100 nm and thickness variations of less than 5% are demanded for high quality coatings. This technique is not commonly used and it is only applicable for smaller substrate sizes. The flat-spray coating technique offers high throughput and uses only "fresh" sol. One example involves forming a PbO-SiO₂ coating containing Au colloids. 100 nm thick layers were obtained that have ruby red to violet colours with peak optical densities up to 2 (Figure 66).
The glass panes were moved from the right to the left on a metallic conveyor belt with an adjustable speed from 0.47 to 1.67 m/min. The coating was applied in a closed spray booth using two high-volume low-pressure spray guns (Krautzberger HVLP), mounted crosswise on one axis. They moved perpendicular to the direction of the substrate transport with a fixed program. A water curtain of about 2 m$^3$ was circulating under the conveyor belt and 7000 m$^3$/h filtered air was flowing in the spray booth for mist control. After passing a flash-off zone the coatings could be dried at temperatures up to 250°C with IR radiation. With optimized sol parameters and spray parameters, the flat-spray technique could be used to get optical coatings with controlled thicknesses in the range of about 200 nm.

2.8.10.4 Doctor blade techniques

Doctor blade or Tape casting is one of the techniques developed in the early 1940s for producing thin films on large surface areas. The doctor blade process involves placing a solution or a well-mixed slurry (consisting, for example, of a suspension of ceramic particles along with other additives such as binders, dispersants or plasticizers) on a substrate beneath the doctor blade. When a constant relative movement is established between the blade and the substrate, the solution or slurry spreads on the substrate to form a thin sheet which results in a uniform layer upon drying. The doctor blading can operate at speeds of up to several meters per minute and it is suitable to coat substrates with a very wide range of wet film thicknesses ranging from 20 to several hundred microns. Typical types of coating devices use either a doctor blade (rectangular frame) or spiral film applicator$^{197}$. 

Figure 66: Scheme of the Venjakob flat spray procedure
For a frame doctor blade, this technique is used in combination with a reservoir. The layer is formed by a doctor blade that is either stationary when used with a moving casting surface, or by a frame that moves along a stationary casting surface. The overall principle is shown below in Figure 67:

![Figure 67: Principle of doctor blading using a frame with a reservoir of coating liquid which is moving relatively to the substrate](image)

The thickness can be modified by adjusting the gap between the doctor blade and the substrate as illustrated in Figure 68 below:

![Figure 68: Wet layer thickness control by the gap between the frame and the blade](image)

Initial experiments involving the casting of the polymer films onto backing materials to make membranes were carried out using the doctor blade approach. A polymer sample made using Method A was cast onto a backing with thicknesses between 50 and 250 µm to determine what might give the best type of membrane.

Variations investigated included

- Casting the polymer without removal of excess solvent.
- Casting the polymer and removing the solvent by immersion in n-hexane
- Casting the polymer and removing the solvent by immersion in deionised water
Images during casting using Elcometer 4340 thin film applicator using a 4340 doctor blade.

After each casting process, the polymer membrane was cured by heating to ensure full polymerization of the CMS. To do this, the membrane was cured in an oven at 85°C for 5 hours\textsuperscript{175}. These trials were carried out on a small scale using glass microscope slides with all the edges sealed with plastic adhesive tape. This is shown schematically Figure 70:

![Figure 69: Elcometer 4340 thin film applicator using a 4340 doctor blade](image)

However, the plastic tape did not properly seal the slides. Hence, in an attempt to overcome this, silicone tubing (id 17 mm; od 20 mm, inert to heat and peroxides) was used to act as an O-ring between the glass slides. It was found that the silicone tubing by itself was not satisfactory since it was squeezed tightly by the glass slides and it was difficult to maintain the required shape. Subsequently, it was found that inserting a Teflon coated copper wire (od 10 mm) into the tubing resulted in the formation of a gasket that retained its shape and also was not easily compressed. The wire incorporated inside the silicone tubing were shaped to make a

![Figure 70: slides cover with brown tap](image)
rigid rectangular gasket which was found to give proper sealing between the glass slides. In the early trials the membrane was held underneath the gasket, but it was found that on heating the membrane crumpled as it expanded and gave a wavy surface.

Therefore in subsequent treatments it was made sure that the membrane was smaller than the size of O-ring. The final design that was used is illustrated schematically below in Figure 71:

![Diagram of the sealing design](image)

Figure 72: Schematic diagram of the best sealing

For a polymer sample made by Method B above, the same casting and curing process as above was used. However, once the casting was done, excess solvent was removed by immersing the membrane in either toluene or acetone.

![Actual images of sealing](image)

Figure 71: Actual images of sealing small scale (left) and actual sealing with big scale (right)
The reason these solvents were used was that both can evaporate easily. Nevertheless, a problem arose when the membrane was immersed in water after immersed in either toluene or acetone. When the cast membrane was immersed in water, flakes of the polymer were observed to be floating on the solvent surface. This was caused by the cast polymer not sticking onto the backing. Therefore, this particular method was not pursued.

Using polymer synthesis Methods C, E and F, the same casting and curing techniques were performed using n-hexane as the immersing solvent. A number of variables such as membrane thickness (50-250) µm, different immersing solvents and different solvents to re-dissolve the solid polymer (DMF and NMP) were investigated. NMP was chosen as the preferred solvent to re-dissolve the polymer because the polymer had a higher solubility in it. For method D, the polymer solution had a viscosity similar to water, and so the doctor blade could not be used. Therefore, the membrane was manually painted onto the backing in a few layers before curing in the oven.

It was subsequently found that the preferred methods of polymer synthesis were methods D and F (section 2.8) and the preferred method of casting was using the Elcometer thin film applicator with doctor blade 4340 (speed 3) followed by immersion in n-hexane to remove any remaining monomer or excess solvent. Lastly the ideal method for curing was to heat cure the polymer film between two glass slides with a rectangular gasket holding them apart at 85 °C for 5 hours, and assembled as in Figure 72.

Once the polymer film had been cast onto the backing and cured it was studied for the presence of pin-holes before proceeding to the next step which involved surface functionalization of the membrane. To do this the membrane was placed on a powerful LED lamp and visually inspected for pin holes. A LED lamp was used as it provided a high intensity of light with minimal heating.

Figure 73: LED lamp to measure pin holes
2.8.11 Summary of different methods of anchoring catalysts to solid supports

Oxidation processes are the most versatile and useful techniques to destroy EDC and pollutants in water. However, traditional oxidation processes have many problems including the production of large amounts of pollutant materials\textsuperscript{200}. Therefore, various researchers for the last decade or two have been focused on replacing heavy metal inorganic oxidants, such as Cr-(VI) and Mn-(VII) as well as chlorine, with a greener oxidation system. One of the emerging replacement oxidants that is commonly being used is hydrogen peroxide. This is because organo-chlorides are not produced as reaction by-products, it is relatively safe to store, cheap and is readily available.

One promising way of providing a green oxidation process is to use hydrogen peroxide as the oxidant in conjunction with a heterogeneous catalyst. Heterogeneous catalysts are superior with respect to facile recovery and recycling\textsuperscript{201} compared to homogenous catalysts. In addition, superior performance can also be achieved by immobilizing one or more components of the catalytic systems onto a large surface area solid carrier to create new organic-inorganic hybrid (interphase) catalysts\textsuperscript{202}. An interphase is defined as a region within a material in which a stationary (organic-inorganic hybrid catalyst) and mobile component (solvent and reactants) penetrate each other on a molecular level. According to the definition, an interphase catalyst is composed of three parts. An inert matrix (support), a flexible organic spacer, and an active centre\textsuperscript{203}. In contrast to traditional heterogeneous catalysts, the interphase organic spacer provides sufficient mobility to the reactive centre and diminishes any undesired steric effect of the matrix over the accessibility of the reactive centre. Therefore, these systems are able to simulate homogeneous reaction conditions, but at the same time they have the advantage of easy separation and recovery of the heterogeneous catalysts.

One of the closest examples to the design of our novel system is reported by Neumann where he developed an aqueous alkene oxidation system using hydrophobic silica particles derivatized with polyoxometalates (POM) as the catalyst\textsuperscript{204}. The purpose of this strategy was to create multifunctionalized, insoluble, silicate-based particles, capable of effective adsorption of alkene reactants and containing reactive centres at the particle and adsorbed substrate-water interface.

Effective adsorption of the substrate was achieved by introducing hydrophobic silicate xerogels with covalently attached phenyl groups. To facilitate the interaction with the catalytic centre, anionic polyoxometalate (POM) and quarternary ammonium cations was included in the
hydrophobic region and were immobilized to the surface of silica. This system was used to catalyse the oxidation of alkenes to epoxides in 30% aqueous hydrogen peroxide in the absence of an organic solvent. Schematic diagrams of the systems are shown in Figure 74:

![Schematic diagram of multifunctionalized catalytic silica](image1)

**Figure 74: Simplified representation of multifunctionalized catalytic silica in hydrocarbon water mixtures**

In addition, Neumann also developed a new immobilized technique for supported, solvent-anchored liquid-phase catalysis\textsuperscript{205}. Polyethers were attached covalently to silica surfaces, and the polymer acted as a solvent and/or a complexing agent for the oxidative catalyst (POM). In this system, the bound polyether catalyst phase was in contact with two immiscible liquid phases: the oxidant (30% aqueous H\textsubscript{2}O\textsubscript{2}) and the organic substrate (cyclooctene). The supported catalyst was at interface where the solubilized reactants come in contact and react.

A schematic diagram is shown below in Figure 75:

![Schematic diagram of supported solvent anchored liquid phase catalytic system](image2)

**Figure 75: Illustration of the supported solvent anchored liquid phase catalytic system**

In addition, to using a POM as a catalyst with the hydrogen peroxide system, Noyori and co-workers recently showed that a combination of Na\textsubscript{2}WO\textsubscript{4}/C\textsubscript{6}H\textsubscript{5}PO\textsubscript{3}H\textsubscript{2} and a quaternary ammonium hydrogen sulfate salt (used as an acidic phase transfer catalyst) could be effectively
applied to the selective oxidation of sulfides to sulfoxides or sulfones using 30% H₂O₂ under halide-free conditions. Despite that, this system still required homogenous conditions which lead to the alteration from using a phase transfer catalyst in Noyori’s protocol to a silica matrix having a quaternary organic spacer. This lead to the discovery of a novel silica-functionalized ammonium tungstate as a recoverable heterogeneous catalyst for the selective oxidation of sulfide to sulfoxides using 30% H₂O₂. The catalyst was simply prepared by building up an aminopropyl group on the surface of commercially available mesoporous silica followed by the acidification of the amino groups using triflic acid and an ion exchange of the triflate ion for the tungstate ion. A schematic diagram of the reaction is depicted below in Figure 76.

![Figure 76: Formation of novel silica-functionalized ammonium tungstate](image)

Since the immobilization of active metal complexes onto solid supports seems to have a promising future, various studies have been implemented to develop a true heterogeneous, stable and recyclable catalyst which affords high epoxidation rates and selectivity which are comparable to their homogeneous counterparts. One interesting example was demonstrated by Neumann and Miller where a silicate xerogel was covalently modified with
phenyl groups and a quaternary ammonium–polyoxometalate ion pairs (Figure 77) was used. The anionic polyoxometalates (POM), \( \{\text{PO}_4\}[\text{W}(\text{O})(\text{O}_2)]_4\}^{3-} \) and \([\text{WZnMn}^{\text{II}}_2\text{ZnW}_9\text{O}_{34}]_2^{12-}\), are the catalytically active species. In addition, the introduction of surface phenyl groups aimed to enhance the hydrophobicity and, thus, the adsorption of the reactant\(^{210}\). On top of that, the combined presence of the phenyl group together with octyldimethyl substituted ammonium salts brings about the maximum catalytic activity.

![Figure 77: Silica xerogel covalently modified with phenyl groups and quaternary ammonium-polyoxometalate (POM) ion pairs](image-url)
2.8.12 Functionalization

To incorporate an Fe-TAML catalyst on the new polymer membrane films that were produced, and to provide “molecular brushes” to concentrate the substrates to be oxidised, the membrane film needs to undergo functionalization. This was carried out by reacting a significant proportion of the chloromethyl groups of the polymer with the long chain amine N,N-dimethylhexadecylamine (LCA) to form quaternary ammonium functions attached to the polymer. The functionalisation was carried out by treating the cast polymer film with the long chain amine in 1,4-dioxane. Once the quaternisation reaction was complete, in most instances the polymer chains were then cross-linked by treatment with 1,6-diaminohexane in 1,4-dioxane solution, and in all cases the functionalised polymer was finally treated with neat diethanolamine to functionalise any remaining chloromethyl groups. A summary of the different functionalisation methods investigated is given in Table 13 below:

<table>
<thead>
<tr>
<th>No</th>
<th>Membranes</th>
<th>Quartenization condition</th>
</tr>
</thead>
</table>
| 1  | PCMS in solvent (DVB +AIBN + xylene + dodecane) | 5 hour in (60:40) N,N-dimethylhexadecylamine in 1,4-dioxane  
5 hour neat diethanolamine |
| 2  | PCMS + DVB (0.5%)+ NMP (try 2 separate quartenization condition) | 5 hour in (60:40) , N,N-dimethylhexadecylamine in 1,4-dioxane  
5 hour in (60:40), 1-6 diaminohexane in 1,4-dioxane  
5 hour in neat diethanolamine  
5 hour in (60:40) , N,N-dimethylhexadecylamine in 1,4-dioxane  
5 hour in neat diethanolamine |
| 4  | Copolymer + DVB (0.5%) +NMP | 5 hour in (60:40) , N,N-dimethylhexadecylamine in 1,4-dioxane  
5 hour in neat diethanolamine |
<table>
<thead>
<tr>
<th>6</th>
<th>5 hour in (60:40), N,N-dimethylhexadecylamine in 1,4-dioxane</th>
<th>5 hour in (60:40), 1-6 diaminohexane in 1,4-dioxane</th>
<th>5 hour in neat diethanolamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5 hour in (60:40), N,N-dimethylhexadecylamine in 1,4-dioxane</td>
<td>5 hour in (60:40), 1-6 diaminohexane in 1,4-dioxane</td>
<td>5 hour in neat diethanolamine</td>
</tr>
</tbody>
</table>

Table 13: Functionalisation methods for the 7 best membranes

After each stage of the functionalization reactions, the membrane was tested using a glass U-tube apparatus (see section 2.10.1) to ensure the polymer membrane was still porous and allowed the buffer solution to slowly diffuse through. This was done by measuring how much solution passed through over a certain time from the permeate side to the retentate side under the action of a standard hydrostatic head of 14 cm of solution. Three U-tube devices with different tube diameters (2.0, 3.0, and 7.0 cm) were employed for these simple tests. To qualitatively measure the relative number of chloromethyl groups that had been functionalised, the IR spectrum of the polymer surface on the PP backing was obtained using an ATR attachment on the FTIR instrument. However after a series of trials, it was discovered that the backing itself gave a background reading in region of interest (800-850 cm\(^{-1}\)). Hence it was quite difficult to compare the success of the functionalization reactions even after taking into account the background reading. To overcome this, a thicker PCMS membrane was cast on a glass slide and after curing was peeled off and functionalised directly (refers section 2.8.12).
Using these techniques, each step of the functionalization process was monitored without interference from the backing material. The IR spectrum of the polymer film was closely studied in the region 800-850 cm\(^{-1}\) as this is the region the \(\delta\)(C-Cl) bands occur.

### 2.8.12.1 ATR-FTIR introduction

FTIR is a technique used to obtain infrared absorption, emission and reflection spectra for molecular species. This technique assumes that all signals arise from various changes in energy brought about by transitions of molecules from one vibrational or rotational energy state to another\(^{211}\). A schematic diagram of FTIR and how the system works is shown below\(^{212}\).

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**Figure 78:** (a) A representation of an FTIR spectrometer and (b) a representation of how the ATR principle works.
To determine the optimum time for each of the functionalization reactions, preliminary experiments were done to measure the time the respective polymers have to be treated with the amine reagents to give the required degree of functionalisation. This was investigated using the PCMS polymer (homo method) as a representative sample and a series of heating tests was carried out for different times (2, 4 or 6) hours with a (60:40) ratio of long chain amine $N,N$-dimethylhexadecylamine: 1,4-dioxane mixture. The band due to $\nu$(C-Cl) was observed in the 800-850 cm$^{-1}$ region of the spectra\textsuperscript{211}

![Figure 79: IR spectrum of PCMS without backing](image)
Figure 80: IR chromatogram of PCMS with 2h quarternized with N,N-dimethylhexadecylamine and 1,4-dioxane in a (60:40) ratio
Figure 81: IR spectrum of PCMS with 5h quartenized with N,N-dimethylhexadecylamine and 1,4-dioxane (60:40) ratio
From this IR results in Figures 80-81 it was decided to use a time of 5 hours to carry out the quarternization step because the goal was to replace most of the chloride groups with quaternary ammonium groups, but at the same time, to still have approximately (10-20)% of un-functionalized groups left to be cross-linked by 1,6-diaminohexane. After this treatment the remaining un-functionalized groups were then end capped by treatment with neat diethanolamine. The result after each step of the functionalization process is shown below using the PCMS polymer as a representative sample. To compare each stage of the functionalization techniques, the IR spectra are shown in the next few pages.

Figure 82: IR chromatogram of PCMS with 5h quarternized with N,N-dimethylhexadecylamine and 1,4- dioxane (60:40) ratio and 1,6- diaminohexane in 1,4- dioxane (60:40) ratio
Polymer on its own refer to Figure 79 while PCMS polymer quartenized with N-N demethylhexadecylamine in 1,4-dioxane shown in Figure 81.

Figure 83: IR chromatogram of PCMS with 5h quartenized with N,N-dimethylhexadecylamine and 1,4-dioxane (60:40) ratio and 1,6-diaminoheksane in 1,4-dioxane (60:40) ratio and neat diethanolamine
2.8.12.5 Introduction to scanning electron microscopy (SEM)

Scanning electron microscopy is based on the secondary emission of electrons\(^\text{213}\). The technique produces images by scanning with a focused beam of electrons. The process starts by providing energy (by a focussed beam) to the atomic electrons present in the solid, making use of the fact that electrostatic or magnetic fields, applied at the right angles to the beam, can be used to change its direction of travel. This allows the formation of secondary electrons which are of various energies and can be detected to provide information about the sample surface, topography and composition. The electron beam is normally scanned simultaneously in two perpendicular directions x and y, a square or rectangular area of specimen (raster scan) can be covered and the secondary electrons that are detected will produce an image\(^\text{213}\). The x-scan is relatively fast while the y-scan is slower provided by the saw tooth-wave generator. Specimens can be observed in various conditions including high vacuum, dry conditions, and over a vast range of cryogenic or elevated temperatures.

In general there are different types of signal that can be observed using SEM including secondary electrons (SE), light (cathodoluminescense) (CL), characteristic X-rays and back-scattered electron (BSE). Secondary electrons in particular result from the interaction of the electron beam near the surface of the samples. This allows for high resolution images to be formed and is typically between 1 nm to 10 nm in diameter\(^\text{213}\). Moreover, due to the narrow electron beam, SEM images have a relatively large depth of focus which provides a three-dimensional appearance of the surface and this is useful for understanding the surface structure of a sample. In addition, a wide range of magnifications is also possible and range from 10 times magnification to more than 500,000 times magnification. A picture of an SEM instrument is given in Figure 84 below:

Figure 84: Schematic diagram of a scanning electron microscope
2.8.12.5.1 SEM result top and on edge view

SEM images of a polymer film (see section 2.11.17) that had been cast onto a backing and then functionalised, cross-linked and finally treated with neat diethanolamine (refer section 2.11.11) are given in Figures 85.

The images in Figure 85 show that on the top side of the backing material where the polymer film was cast, the surface is rough on the 50 – 100 µm scale. In the image on the right it can be clearly seen that some of the rough surface material has been lost next to the edge of the backing where the sample had been cut. This has exposed the top surface of the backing and some of the fibers of the backing material can be clearly seen. However, it is important that the image shows the voids between the fibres have been essentially filled with the cast polymer, as would be expected.

Figure 85: SEM images of PCMS anchored with Orange (II) dye at 2 different spot on the same smart film (top view)
In contrast to this, the images of the underside of the same coated backing material (see Figure 86) clearly show the compressed fibers of the backing material with a small amount of the polymer coating having penetrated completely through the backing material to the underside when it was cast.

Using a microtome at liquid nitrogen temperature, the edge of the same polymer-coated backing material was cut in an attempt to remove thin sections that could be analysed. Unfortunately, suitable thin sections could not be obtained. However, images of the edge remaining after these cutting attempts were obtained and these are given in Figures 87 and 88. In Figure 87 the edge is shown exactly perpendicular to the viewing direction. In Figure 88 the edge is tilted slightly so the underside of the membrane is just visible. Importantly these images show that the cast polymer has essentially penetrated through most of the thickness of the backing with a clear build-up of polymer on the surface to which the polymer was applied. There are very few voids at all in the coated backing material.
Attempt were also made using EDX-SEM to measure distribution of Fe within the composite polymer membrane. Unfortunately, the amount of adsorbed iron catalyst was too small to be detected.
2.8.12.6 TEM intro

Transmission electron microscopy is based on the principle that when electrons penetrate a thin specimen they can then be focused by appropriate lenses to give images of the sample, in broad analogy with the optical microscope. A picture of a typical modern TEM instrument is provided in Figure 89.

Figure 89: Images of Technai FEG20 TEM

TEM is capable for imaging with magnification in the range of $10^3$ to $10^6$ which is mainly caused by de Broglie electrons (shown below) which lead to the specimen to be examined in fine detail.

$$\lambda_e \approx \frac{\hbar}{\sqrt{2m_0E\left(1 + \frac{E}{2m_0c^2}\right)}}$$

Equation 23: De Broglie Equation

In this equation $\hbar$ is Planck’s constant, $m_0$ is the rest mass of an electron and $E$ is the energy of the accelerated electrons. Electrons are generated from a process known as thermionic emission from a filament, normally tungsten or alternatively by field electron emission. The electrons are then accelerated by an electric potential and focused by electrostatic and electromagnetic lenses onto the sample. The transmitted beam which contains information about electron density, phase and periodicity used to form an image.
In addition, the instrument can be used to produce electron-diffraction patterns, useful for analysing the properties of crystalline specimens. Overall a TEM instrument can be divided into 3 broad sections; the illumination system, specimen stage and imaging system.

2.8.12.6.1 TEM result

Attempts were made to obtain TEM images of the polymer-coated backing materials. The TEM images were obtained at low magnification while being supported on carbon film. The polymer-coated backing materials were set in resin and attempts made to obtain edge sections of the composite material by making transverse cuts with a microtome. However, problems were encountered as the cutting process pushed the backing fibers through the encasing polymer material to leave artificial voids. This can be seen clearly in Figures 90. In Figure 90 the circular or elliptical shapes are the cut fibers and the “fiber-shaped” voids left after many of these have been pushed through the encasing polymer matrix during cutting are indicated. This displacement of the fibers remained a problem even when a cryo-ultramicrotome was used to cut the specimens. In addition, EDX-TEM was also carried out on the thin sections obtained, but no significant results could be obtained due to the very small amount of Fe present from the adsorbed Fe-TAML catalyst.
Low resolution images

Figure 90: TEM images of PCMS + DVB low magnification at different spot
2.8.12.7 Monitor surface area using Leica DMR research microscope (2 system)

Microscopy in broad terms can be divided into three categories: optical, electron and scanning probe microscopy. Optical or light microscopy involves using visible light transmitted through or reflected from the sample through a single or multiple lenses to allow a magnified view of the sample. The resulting image can be detected directly by the eye, imaged on a photographic plate or captured digitally\textsuperscript{215}. Even though optical microscopy is the most up to date methodology, these techniques still have several limitations. Firstly, this technique can only observe dark images effectively.

Secondly, the diffraction limits the resolution to approximately 0.2 micrometres and thirdly, out of focus light from points outside the focal plane reduces the image clarity. Thus to overcome these constraints and to improve specimen contrast or to highlight certain structures in specimen, various techniques can be employed including bright and dark field, phase contrast, differential interphase contrast (DIC) and lastly fluorescence imaging.

![Leica DMR research microscope](image)

Figure 91: Leica DMR research microscope
**Samples:** PCMS using the solventless method (removed TBC), 50 µm thickness.

![Image](image1.png)

*Figure 92: No fluorescence, 20 times magnification, 24.6 ms exposure time filter 2 (left) and fluorescence filter 2, 20 times magnification, and 18.4 ms exposure time (right)*

**Samples:** PCMS using the solventless method (removed TBC), very thick without backing film coated with Orange (II) dye.

![Image](image2.png)

*Figure 93: No fluorescence, 20 times magnification, 38.1 ms exposure times LHS, Filter 2, 20 times magnification, 474.0 ms exposure times (middle) and Filter 2, 20 times magnification, 94.6 ms exposure times*
**Samples**: PCMS +0.5% DVB using the solventless method (removed TBC) with Orange (II) with backing

![Figure 94: No fluorescence, 20 times magnification, 13.5 ms exposure time (left) and Fluorescence filter 2, 20 times magnification, 18.4 ms exposure time (right).](image)

**Samples**: PCMS + 0.5% DVB using the solventless method (removed TBC) no backing

![Figure 95: 10 times magnification, no filter, 60.8 ms exposure time (left) and filter 2 fluorescence, 101.3 ms exposure time (right).](image)
2.8.12.8 Confocal laser microscope (CLM)

CLSM is a technique that generates clear, thin optical sectioned images, totally free out-offs focus fluorescence. The principles of laser microscopy were first discovered by Marvin Minsky in 19/5/72216. Not only does this technique provide remarkable optical sectioned fluorescence images in a matter of seconds, but it also provides x-z sections (providing views at right angles to the normal direction of observation) which can also be captured and rapidly displayed on the monitor. In addition, a series of optical sections (stored in the memory of the built-in or add-on digital image processor) can be converted into 3D images or displayed as stereo pairs216.

![Schematic diagram of laser scanning confocal microscope](image)

For opaque specimens, this is useful for surface profiling, while for non-opaque specimens, interior structures can be imaged. For interior imaging, the quality of the image is greatly enhanced due to the fact that information from multiple depths in the specimen is not superimposed214. Compared to conventional microscopes that can observe as far into the specimen as the light can penetrate, confocal microscope on the other hand can only observe images at one depth at a time217. The microscope that was used for this work is known as the Andor revolution spinning disc confocal microscope. This imaging system is optimised for long-term and/or high speed imaging of a specimen. The spinning disc confocal system allows for faster imaging and lowers overall illumination levels than is practical with conventional point scanning confocals. Four laser lines (violet, blue, green and red) and a wide range of emission filters offer flexibility in the design of experiments. The iQ software allows complex experimental designs to be accommodated. Standard wide field fluorescence and bright field
imaging are also well catered for. The system is hosted on a Nikon Ti-E inverted microscope. Characteristics are as for our standard (non-confocal except that the confocal has in addition: motorised X-Y stage; piezo Z stage; Perfect Focus system; and an incubator cabinet that allows for temperature regulation and control of CO$_2$ supply to the specimen).
2.8.12.8 CLMS result Image of 50 µm thickness PCMS+ 0.5% DVB membrane immersed in Orange (II)

Figure 97: Image of 250 µm thickness PCMS+NMP membrane immersed in Orange II (200 µM in 100mL) LHS and Image of 250 µm thickness Copolymer+ 0.5% DVB membrane immersed in Orange II (200 µM in 100mL) RHS

Figure 98: Image of 50 µm thickness Copolymer+ 0.5% DVB membrane immersed in Orange II (200 µM in 100mL) LHS in green region and RHS is the same membrane in Orange region

Figure 99: PCMS+ 0.5% DVB membrane immersed in Orange II (200 µM in 100mL) LHS in green region and RHS is the same membrane in Orange region.
2.90 Anchoring the catalyst molecules on the smart films

Once the smart film was prepared, the next step was to investigate if the oxidation catalyst could be successfully anchored onto the smart film. If this final step succeeded, the resulting smart catalytic film could then be evaluated further with respect to leaching of the catalyst and its operation in oxidation processes. An important point to confirm was that catalytic oxidation was carried out by the catalyst anchored onto the smart catalytic film rather than catalyst leached into the aqueous solution which would result in homogeneous catalytic oxidation.

The oxidation catalyst FeB* was chosen as the catalyst that would be investigated in initial experiments. Attachment of this catalyst was carried out by immersing a membrane (PCMS + NMP, 35 mm) in aqueous Fe-TAML solution (20.0 mL, 50 µM, 1.0 µmole FeB*) overnight. The next day the membrane was removed, washed and immersed on a wire support in fresh carbonate buffer solution (20.0 mL, 0.01 M, pH 9.5) and stirred for 15-20 min. The membrane was then removed, washed and transferred to another fresh carbonate buffer solution where it remained for a further 15-20 min. This procedure was repeated a further two times. The amount of FeB* catalyst that remained unadsorbed from the original solution of FeB*, plus the amounts that were leached into solution after each immersion in the buffer solutions were then measured. To do this, the small amounts of FeB* in each of the solutions were used to catalyse the oxidation of the dye orange II with hydrogen peroxide under standard conditions tabulated in Table 14.

<table>
<thead>
<tr>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Orange (II)]</td>
</tr>
<tr>
<td>50.0 µM</td>
</tr>
</tbody>
</table>

Table 14: Standard bleaching condition

In each case the initial rate of oxidation (bleaching) of the dye was measured using an Ocean Optics UV-vis spectrophotometer. From these initial rates the concentration of FeB* in each of the solutions could be determined by reference to a calibration curve of reaction rate vs FeB* concentration under these same conditions that was obtained separately. The results obtained for the original solution of FeB* that remained after the membrane was removed and the four buffer solutions are presented in Table 15.
Table 15: Bleaching run to measure leaching of Fe-(TAML) in buffer solution

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Initial rate (mol L^{-1}s^{-1})</th>
<th>Residual [Fe-TAML(FeB*)] in solutions</th>
<th>Number of moles of FeB* in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original FeB* in buffer solution</td>
<td>9.419 x 10^{-7}</td>
<td>2.94 µM</td>
<td>0.059 µmole</td>
</tr>
<tr>
<td>Buffer solution after 1st immersion of membrane</td>
<td>5.015 x 10^{-7}</td>
<td>1.47 µM</td>
<td>0.030 µmole</td>
</tr>
<tr>
<td>Buffer solution after 2nd immersion of membrane</td>
<td>1.747 x 10^{-7}</td>
<td>0.38 µM</td>
<td>0.008 µmole</td>
</tr>
<tr>
<td>Buffer solution after 3rd immersion of membrane</td>
<td>Not measurable</td>
<td>Not measurable</td>
<td>Not measurable</td>
</tr>
</tbody>
</table>

The results show that in total, 0.903 µmole of FeB* remains adsorbed onto the membrane after the above treatments. This corresponds to 90.3% of the 1.0 µmole present in the original solution. Furthermore, the amount of FeB* leached from the membrane during each consecutive immersion in the buffer solutions decreases until the amount leached in the 3rd cycle is too small to measure (i.e. is < 0.0004 µmoles).

In addition, the adsorption of FeB* onto the smart film could be observed visually if sufficiently high amounts of FeB* were adsorbed and an example of this is shown in Figure 100. In this case approximately 2.0 µmole of FeB* were adsorbed onto the film. One feature of this film (and this was common to most of the films produced) was that visually it did not appear the catalyst was distributed completely evenly over the surface of the film with darker and lighter orange regions clearly visible. Producing films that had a more even distribution of catalyst is one goal for future studies.
Figure 100: smart film on left hand side and smart catalytic film on the right hand side
2.10 Choice of the best membranes for further study

In order to determine which smart catalytic films showed the most promising performance, preliminary tests were carried out to measure the permeability and catalytic oxidation characteristics of the films. From the results of these tests, which are discussed below, three of the most promising films were chosen for more detailed studies. The results of these studies are presented in Chapter 3.

In order to estimate the permeability of the membranes, each membrane was tested with aqueous carbonate buffer solution after each stage of the smart thin film production, starting with virgin backing (PP), the CMS polymer on the PP backing, the film after the polymer film had been quartenized with the N,N-dimethylhexadecylamine, the film after cross-linking with 1,6-diaminohexane and lastly the film after end capping with diethanolamine. These tests were carried out using a “U-tube” glass device which had a joint in the middle section into which the polymer film could be clamped. The flow of solution from one side to another was driven by the hydrostatic pressure in one arm of the U-tube generated by the solution in that arm being higher than in the other arm.

Schematic diagram of the u-tube glass device are shown below in Figure 101:

![Figure 101: Schematic diagram of U-tube glass apparatus](image-url)
The type of polymer films that underwent permeability testing are summarized in table 16

<table>
<thead>
<tr>
<th>Membrane no</th>
<th>Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCMS + solvent (DVB+ AIBN+ xylene+ dodecane)</td>
</tr>
<tr>
<td>2</td>
<td>PCMS + 0.5% DVB + NMP</td>
</tr>
<tr>
<td>3</td>
<td>Copolymer + DVB 0.5% + NMP</td>
</tr>
<tr>
<td>4</td>
<td>Copolymer + NMP</td>
</tr>
<tr>
<td>5</td>
<td>Emulsion polymer</td>
</tr>
<tr>
<td>6</td>
<td>PCMS + NMP</td>
</tr>
</tbody>
</table>

Table 16: Types of membranes that undergo permeability test

To carry out these experiments the membrane to be tested was placed between the joint in the U-tube and clamped tightly to ensure no leaking occurred. Then, 100 mL of carbonate buffer (0.01 M, pH 9.5) was then placed in one arm of the U-tube and 30 mL in the other arm. This gave a height differential between the two sides of 14 cm. The heights were then monitored to see how long it took for the height of solution in each arm to become the same, or alternatively, the volume of buffer solution the permeated through the film in a set time (30 min – 60 min). This was done to all the membranes at each stage of production. For these screening tests, polymer films of 100 µm were used. For the virgin backing, the heights of the carbonate buffer reached equilibrium within 1-2 min. This illustrates that the PP backing itself was very porous.
2.10.1 Preliminary test involving permeability with U-tube glass apparatus

The results are summarized in Table 17 in terms of time to reach equilibrium:

<table>
<thead>
<tr>
<th>Entry</th>
<th>After casting 2 layers (nominally 100 µm)</th>
<th>N,N-dimethylhexadecylamine</th>
<th>1,6-diaminohexane</th>
<th>Neat diethanolamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15 minute</td>
<td>20 minute</td>
<td>25 minute</td>
<td>30 minute</td>
</tr>
<tr>
<td>2</td>
<td>15 minute</td>
<td>20 minute</td>
<td>25 minute</td>
<td>30 minute</td>
</tr>
<tr>
<td>3</td>
<td>15 minute</td>
<td>20 minute</td>
<td>25 minute</td>
<td>30 minute</td>
</tr>
<tr>
<td>4</td>
<td>20 minute</td>
<td>25 minute</td>
<td>30 minute</td>
<td>40 minute</td>
</tr>
<tr>
<td>5</td>
<td>10 minute</td>
<td>15 minute</td>
<td>20 minute</td>
<td>20 minute</td>
</tr>
<tr>
<td>6</td>
<td>20 minute</td>
<td>25 minute</td>
<td>30 minute</td>
<td>40 minute</td>
</tr>
</tbody>
</table>

Table 17: Summary of permeability experiment with u-tube

From the data in the table above, the average flow rate of solution permeating through the polymer film can be determined and the results are indicated in Table 18:

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Flow rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2 mL/min</td>
</tr>
<tr>
<td>2</td>
<td>1.2 mL/min</td>
</tr>
<tr>
<td>3</td>
<td>1.2 mL/min</td>
</tr>
<tr>
<td>4</td>
<td>0.9 mL/min</td>
</tr>
<tr>
<td>5</td>
<td>1.75 mL/min</td>
</tr>
<tr>
<td>6</td>
<td>0.9 mL/min</td>
</tr>
</tbody>
</table>

Table 18: Summary of flow rate (mL/min) for respective smart films 100 µm thickness
These results show that the flow rate of solution through the polymer films of 100 µm thickness range from 0.9 mL/min to 1.75 mL/min, which is quite fast. It was suspected that this fast flow rate was probably due to the existence of pin holes and indeed examination of the films illuminated from underneath showed some very small areas where the coverage was probably not the same as in other areas. Hence, to overcome this deficiency, polymer films were then constructed by coating the backing with five separate 50 µm layers of polymer, each layer being heat treated to cure the polymer before the next layer was cast to give a final nominal thickness of 250 µm. Using polymer films constructed in this way, low permeation rates of solution were obtained as shown in Table 19. Polymer films of this thickness and constructed this way were used for most of the more detailed studies that were carried out on the smart catalytic films.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Flow rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.27 mL/min</td>
</tr>
<tr>
<td>3</td>
<td>0.29 mL/min</td>
</tr>
<tr>
<td>6</td>
<td>0.21 mL/min</td>
</tr>
</tbody>
</table>

Table 19: Summary of Flow rate (mL/min) for 3 best smart films nominally 250 µm thick

2.10.2 Preliminary tests involving bleaching with the catalytic polymer films
The second criterion that was used to choose the membranes was performance during dye bleaching reactions where the bleaching reaction was carried out in a beaker with the catalytic film in contact with a buffer solution containing both the dye and the hydrogen peroxide oxidant (Figure 103). In this system, the bleaching was done by adding the smart thin film with anchored FeB* catalyst (1µmole, M_r of FeB* used was 667.32, this was the corrected molar mass given by GreenOx for this sample which accounts for the impurities present), H_2O_2 (1.0 mM), Orange (II) dye (50 µM) and carbonate buffer 20 mL, (0.01 M, pH 9.5). The absorbance of the solution was monitored at 3 min intervals by UV-vis spectroscopy using an Ocean Optics DA spectrophotometer.
Figure 103: Support for the SCFs when catalysing bleaching in a beaker

Figure 104: The Ocean Optics DA UV-vis spectrophotometer used to monitor the absorbance of the solutions while bleaching was occurring.
Before actual bleaching studies were carried out, a blank reaction was performed where the oxidation of Orange (II) was carried out in the presence of hydrogen peroxide, the functionalised polymer, but no FeB*. The results are shown in Figure 105:

![Figure 105: Plot of Absorbance vs time for blank reaction with 1.0 mM H₂O₂ and SF](image)

Within the 70 minute time interval of the reaction, the absorbance only dropped from 1.0 to 0.8. This shows that without the catalyst FeB*, very little drop in the absorbance of the Orange II dye solution occurs. The observed small decrease in absorbance was probably due to some adsorption of the dye onto the SF.
The preliminary bleaching results obtained for each SCF is discussed below:

Experiment 1

The film prepared was prepared from the copolymer + 0.5% (w/w) DVB and cast as an NMP solution. This membrane was prepared and functionalized using N,N-dimethylhexadecylamine, cross-linked using 1,6-diaminohexane, and end-capped with diethanolamine as described previously in section 2.8.12 and then used for the bleaching reactions using the method explained in section 2.9 after FeB* (1.0 µmole) had been adsorbed onto it. All the bleaching experiments were repeated at least 5 times (i.e. the same membrane was used without recharging with FeB*) to provide an estimate of the amount of catalyst decomposition that occurs during each run, 5 consecutive bleaching experiments were carried out and the results are shown on Figure 106.

![Figure 106: Plot of Absorbance vs time (min) CODVBNMP with (3WQ), 5 consecutive bleaching experiments](image-url)
Experiment 2

The film was prepared from PCMS and cast as an NMP solution. This film was functionalised using N,N-dimethylhexadecylamine, cross-linked using 1,6-diaminohexane, and endcapped with diethanolamine as described previously. It was then used for the bleaching reactions using the method explained in section 2.9 after FeB* (1.0 µmole) had been adsorbed onto it. 10 consecutive bleaching experiments were carried out and the results are shown on Figure 107.

![Plot of Absorbance vs time](image)

*Figure 107: Plot of Absorbance vs time (min) PCMSNMP repeated 10 consecutive bleaching experiments*
Experiment 3

The film prepared was prepared from PCMS with 0.5% DVB and cast as an NMP solution, the film was functionalized using N,N-dimethylhexadecylamine in 1,4-dioxane, and neat diethanolamine. It was then used for the bleaching reactions using the method explained in section 2.9 after FeB* (1.0 µmole) had been adsorbed onto it. Since DVB was added as a cross-linking agent before polymerisation, the polymer was not cross-linked after casting by treatment with 1,6-diaminohexane. 10 consecutive bleaching experiments were carried out and the results are shown on Figure 108.

Figure 108: Plot of Absorbance vs time (min) PCDVNMM2 10 consecutive bleaching experiments
**Experiment 4**

The film prepared was prepared from copolymer (1:1 styrene: CMS) with 0.5% DVB and cast as an NMP solution. The film was functionalized using N,N-dimethylhexadecylamine in 1,4-dioxane, and neat diethanolamine. It was then used for the bleaching reactions using the method explained in section 2.9 after FeB* (1.0 µmole) had been adsorbed onto it. Since DVB was added as a cross-linking agent before polymerisation, the polymer was not cross-linked after casting by treatment with 1,6-diaminohexane. 10 consecutive bleaching experiments were carried out and the results are shown on Figure 109.

![Figure 109: Plot of Absorbance vs time (min) for CODVNMP 10 consecutive bleaching experiments](image-url)
Experiment 5

The film prepared was prepared from PCMS with 0.5% DVB and cast as an NMP solution. This film was functionalised using N,N-dimethylhexadecylamine, cross-linked using 1,6-diaminohexane, and endcapped with diethanolamine as described previously. It was then used for the bleaching reactions using the method explained in section 2.9 after FeB\(^*\) (1.0 µmole) had been adsorbed onto it. Since DVB was added as a cross-linking agent before polymerisation, the polymer was not cross-linked after casting by treatment with 1,6-diaminohexane before 10 consecutive bleaching experiments were carried out and the results are shown on Figure 110.

Figure 110: Plot of Absorbance vs time PCMSDVNM 10 consecutive bleaching experiments
Experiment 6

The film prepared was prepared from emulsion polymerization with 0.5% DVB and cast as an NMP solution. This film was functionalised using N,N-dimethylhexadecylamine, cross-linked using 1,6-diaminohexane, and endcapped with diethanolamine as described previously. It was then used for the bleaching reactions using the method explained in section 2.9 after FeB* (1.0 µmole) had been adsorbed onto it before 10 consecutive bleaching experiments were carried out and the results are shown on Figure 111.

![Plot of Absorbance vs time for emulsion polymerization membrane, 10 consecutive bleaching experiments](image-url)

Figure 111: Plot of Absorbance vs time (min) for emulsion polymerization membrane, 10 consecutive bleaching experiments
The blank experiment showed that in the presence of the polymer film and hydrogen peroxide alone the orange II dye is not bleached to any appreciable extent over 30 minutes. In contrast, the orange II is bleached completely within this time when the polymer films contained the immobilised FeB* catalyst. This indicates that in all cases the immobilised FeB* is still accessible to the reagents and can catalyse dye oxidation. However, as would be expected the rate of catalytic oxidation is considerably slower than in the case where the same number of moles of FeB* are present in solution as a homogeneous catalyst (i.e. the FeB* is not immobilised). In the corresponding homogeneous reaction with the same number of moles of FeB* present, the orange II is completely bleached in 3-5 minutes. In each of these experiments the mole ratio of catalyst (FeB*) to orange II was 1:1 for the first bleaching reaction. However, since the bleaching was repeated 10 times (without recharging the FeB*), the reaction is clearly catalytic. In addition, Experiment 1 was stopped after 5 cycles since the fifth run took more than 2 times longer to complete than the first experiment. This indicates that this film was not a good candidate to pursue further. One of the most common problems encountered with immobilised catalysts is that they leach from the solid support during catalytic reactions. Experiments were carried out to address this issue with the SCFs but details of these results are given in Chapter 3.

For the bleaching reactions involving each of the 6 different smart polymer films described above, the reaction conditions were identical and the amount of adsorbed FeB* catalyst was the same (1.0 µmole). In each case the dye was completely oxidised by the immobilised FeB* catalyst. However, there were considerable differences the performance of the catalyst on the different polymer films. In the first catalytic oxidation cycle the time it took for complete bleaching of the orange II varied from about 12 minutes to 22 minutes. Furthermore, when the same film was used for repeated oxidation cycles, in all cases the time it took for complete bleaching slowly increased. After 10 cycles the time for complete bleaching varied from about 15 minutes in some cases through to more than 35 minutes in others. This indicates that during these bleaching cycles the immobilised FeB* is slowly degrading, but that the amount of degradation depends strongly on the nature of the polymer film.

The three polymer films that resulted in the fastest bleaching rate and, importantly, gave the least variation in the rates of bleaching between cycles 1 and 10 were those used in experiments 2, 4 and 5 above. These same polymer films gave relatively slow permeation rates of buffer solution (see Table 19) and so these particular films were selected for more detailed studies and these are described in Chapter 3.
2.11 Experimental procedures

2.11.1 Synthesis of the PCMS polymer using solvent

A typical polymer was prepared from CMS, (0.5-2) % divinylbenzene (DVB) (mol DVB vs mol CMS), 2% Kraton G6932/G6945 (wt% vs CMS), 40% (v/v) diluent containing 2:1 by volume xylene: dodecane. The DVB level was calculated assuming 50% purity for the commercial product. A small quantity of benzyol peroxide was used to initiate free-radical polymerization. In a typical reaction Kraton G6945 (0.110 g) and benzyol peroxide (BPO) (0.040 g) were dissolved in a mixture of VBC (5.0 mL), DVB (0.2 mL), xylene (2.3 mL) and dodecane (1.1 mL) in a conical flask. The flask was plugged with cotton wool and the mixture heated in an oil bath at 85°C until the viscosity reached 600-800 centipoise (8-24 hours). In variations of this procedure, the percentages of Kraton were varied from 0.5% to 4%, BPO from 0.5% to 4%, and azobisisobutyronitrile (AIBN) was used in place of BPO.

2.11.2 Synthesis of PCMS using no solvent

In a typical procedure the inhibitor present in the CMS was first removed by treatment with aqueous NaOH. CMS (7.5 mL) was placed in a separating funnel and NaOH (7.5 mL, 0.5% w/w) added. The separating funnel was gently shaken, the NaOH solution removed and the treatment with the NaOH solution repeated two further times. The CMS was washed with deionized water until the water was neutral. The inhibitor-free CMS was then dried by standing over anhydrous K2CO3 and collected by filtration. The purified CMS (6.5 mL) was then added to a clean Schlenk tube, placed under a nitrogen atmosphere and heated in an oil bath at 85 °C until the solution became viscous. In variations of this procedure, either the radical initiator AIBN (0.5% w/w) alone was added, or DVB (0.5% w/w) either alone or with AIBN (0.5% w/w) was added. After cooling to ambient temperature, the viscous polymer was dissolved in MEK (5.0 mL) and then precipitated by addition of methanol, or alternatively ethanol.

2.11.3 Synthesis PCMS by emulsion polymerisation

CMS (60 g) and methyl acrylate (20 g) were added into a clean conical flask containing deionized water (175 mL), sodium lauryl sulfate (20 mL of a 20% (w/v) aqueous solution), NaHCO3 (9.6 mL of a 5% (w/v) aqueous solution), and K2S2O8 (9.6 mL of a 5% (w/v) aqueous solution). In some syntheses DVB (0.05, 0.3 or 1.0% (% w/w vs CMS) was also added. The ingredients were then cooled in an ice bath for one hour after which time Na2S2O5 (6.8 mL of 5 % (w/v) aqueous solution) was added. The conical flask was then sealed with a septum and
purged with nitrogen for 20 minutes while still in the ice bath. The conical flask was then slowly stirred with a magnetic stirrer (ca. 30-50 rpm) at 25 °C for 3 days. The resulting polymer solution was applied to the backing materials by painting or spraying, with drying between applications of multiple coats (approximately 5-10 coatings).

2.11.4 Syntheses of CMS/Styrene copolymers using (1:1 mole ratio of CMS: Styrene) using a solvent.

The inhibitors were first removed from the both styrene and CMS using the procedure detailed in section 2.11.2, except that (2.5% w/w) aqueous NaOH solution was used to treat the styrene. Inhibitor free CMS (2.5 mL) and styrene (2.5 mL) were added to a conical flask, followed by dodecane (1.1 mL) and xylene (2.3 mL), and finally either AIBN (0.025 g) or BPO (0.025 g). The flask was plugged with cotton wool and the mixture heated in an oil bath at 85°C until the viscosity reached 0.035 Pa.s. After cooling to ambient temperature, the viscous polymer was dissolved in MEK (5.0 mL) and then precipitated by addition of ethanol, or alternatively methanol.

2.11.5 Synthesis of CMS/Styrene copolymers using (1:1 ratio of CMS: Styrene) using no solvent (i.e. homopolymerization)

The inhibitors were removed from both styrene and using the procedure described in Method 2.11.4. Inhibitor-free CMS (5 mL) and styrene (5 mL) were added to a clean schlenk tube, placed under a N₂ atmosphere and heated in an oil bath at 85°C until the solution became very viscous. In variations of this procedure, the radical initiator AIBN (0.5% w/w) alone, AIBN (0.5% w/w) and DVB (0.5% w/w), or just DVB (0.5% w/w) were added before heating. After cooling to ambient temperature, the viscous polymer (0.035 Pa.s), was dissolved in MEK (5.0 mL) and then precipitated by addition of ethanol, or alternatively methanol.

2.11.6 Synthesis of PCMS polymer using toluene

A typical polymer was prepared by adding CMS (6 mL) (without the inhibitor removed) (TBC), toluene (5 mL) and benzoyl peroxide (0.5%v/v) to initiate free-radical polymerization in a clean schlenk tube which was placed under a N₂ atmosphere and heated in an oil bath at 85°C until the solution became viscous. After cooling to ambient temperature, the viscous polymer was added to excess n-hexane (250 mL) and stirred to obtain solid polymer as white flakes.
2.11.7 Methods of casting the polymer on either polypropylene (PP) or polyester (PE) backing

The polymer (formed using the procedures indicated above) was either cast as a viscous liquid directly from the polymerization reaction, or cast as a solution of the precipitated polymer dissolved in NMP. In all cases the polymer was cast as a thin film of thickness 50 μm on a backing and then immediately immersed in a liquid such as water or hexane to remove the excess solvent from the polymer film.

In a typical casting experiment the precipitated polymer (0.7 g) was dissolved in NMP (10 mL) and the viscous solution cast as a thin film (50 μm thick) onto a polypropylene backing sheet (15 cm by 15 cm) using an Elcometer 4340 thin film applicator incorporating a 4340 doctor blade. The casting speed was set at speed 3 (20 mm s⁻¹). The cast film and backing were then immediately immersed in a bath containing n-hexane (200 mL) at ambient temperature and left to stand for 1 hour. After this time the coated backing was removed and the excess solvent allowed to evaporate. In the case of the emulsion polymerised product, the solution was not viscous enough to use the thin film applicator and so the solution was painted onto the backing. After drying for 15-20 minute further coats of polymer were added.

2.11.7.1 Properties of selected backing membranes

PP 2471 nd membrane

<table>
<thead>
<tr>
<th>Type</th>
<th>Novatexx 2471</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Bonding type</td>
<td>Thermal</td>
</tr>
<tr>
<td>Weight</td>
<td>85 g/m²</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.18 mm</td>
</tr>
<tr>
<td>Air permeability at 200 Pa</td>
<td>150 I/m²/s</td>
</tr>
<tr>
<td>Max tensile strength</td>
<td>Long 25%</td>
</tr>
<tr>
<td></td>
<td>trans 30%</td>
</tr>
<tr>
<td>Roll width</td>
<td>Max. 2100 mm</td>
</tr>
</tbody>
</table>

Table 20: Properties of polypropylene (PP) 2471 nd membrane
Composition: 100% Polyester

Characteristics: Fiber Lock Down, Thermally Stable

Applications: Membrane support

<table>
<thead>
<tr>
<th>Grade</th>
<th>84sp1</th>
<th>CU 414</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis Weight</td>
<td>(gsm)</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>(lbs./1300 ft²)</td>
<td>22.5</td>
</tr>
<tr>
<td>Caliper @ 7.3 psi</td>
<td>(mil)</td>
<td>4.0</td>
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<tr>
<td></td>
<td>(mm)</td>
<td>0.102</td>
</tr>
<tr>
<td>Tensile strength MD/CD</td>
<td>(N/25 mm)</td>
<td>122/57</td>
</tr>
<tr>
<td></td>
<td>(kg/in)</td>
<td>12.4/5.8</td>
</tr>
<tr>
<td>Porosity</td>
<td>(cfm/ft² @ 0.5” H₂O)</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>(l/m2/s @ 200PA)</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 21: Properties of polyester (PE) backing membrane²¹⁸

2.11.8 Curing procedures

After the solvent has evaporated from the cast polymer film the polymer film was then cured by heat treatment. In a typical experiment the coated backing was placed between two glass sheets separated by a continuous silicone gasket and very lightly clamped together. The gasket, which was approximately 30 mm thick, completely enclosed the coated backing without touching it. The gasket that was used consisted of silicon tubing (id 17 mm; od 20 mm) into which Teflon insulated copper wire (od 10 mm) was inserted. This allowed the gasket to be formed into the same shape as the coated backing and for the two ends of the gasket to be joined together. The gasket kept the two glass sheets sufficiently separated so that there was approximately (15-20 mm) space between the coated backing and the top sheet of glass. The assembly was then heated in an oven, at 85°C for 5 hours.
2.11.9 Multiple coating procedures

After heat-curing the polymer coating, the sheet could be coated again with another polymer film using the same casting technique described in section 2.11.7. The coating and curing process could be carried out multiple times to build up the thickness of the cured film. In a typical procedure, the backing was coated with a 50 μm thick polymer film and cured 5 times. This gave a polymer film that is described here as being 250 μm thick although the actual thickness was not measured and would be expected to be less thick than this due to shrinkage during solvent removal and curing.

2.11.10 Typical GPC/Chromatogram procedures

The mobile phase solvent for GPC analysis was pure THF filtered through a Teflon filter (TYPE FH, 0.5 μm, Millipore) with a glass filter apparatus. Precipitated PCMS polymer flakes (2 - 4.8 mg) were dissolved in THF (1.0 mL) and filtered through a 0.22 μm nylon syringe filter before analysed on a GPC system consisting of an automatic sampler (Viscotek TDA max) with a dual piston pump of the GPC max, A “Tetra Detector Array” (Viscotek) consisting of light scattering detector, viscometer detector, refractive index (RI) detector and UV detectors. The detectors were connected in series with the RI following the viscometer because of back-pressure limitations on the RI flow cell. The mobile phase was pumped through the column at 1.0 mL/min. Columns were 3x T600M column by Malvern Industries ltd (column size 300 mm long x 7.8 mm ID, guard column 10 mm long x 4.6 mm ID) operated at 35°C. Injection volume was 200 μL and the samples were run overnight before being analyzed using the Omnisec software v 4.70 package. Calibration was with polystyrene standards dissolved and run in THF.

2.11.11 Typical method to functionalize Smart thin films

(A) Functionalization of the polymer with “molecular brushes” and quaternary ammonium groups

Functionalization of the polymer was achieved through treatment of the chloromethyl groups with appropriate reagents that result in the formation of “molecular brushes.” These impart to the porous polymer film the ability to collect and concentrate target species from bulk solution as well as providing the means by which the catalyst can be anchored to the polymer. In a typical experiment the polymer film was treated with a long-chain tertiary amine which reacts with chloromethyl groups converting them into quaternary ammonium functions. Conditions investigated include elevated temperatures, using the reagent either neat or with added solvent, and reaction times of 2-8 hours. Preferred conditions involve heating the coated membrane with
N,N-dimethylhexadecylamine (60 v/v % in 1,4-dioxane) at 85°C for 5 hours in a conical flask with cotton wool. In this way the majority of the chloromethyl groups were converted to –[CH$_2$N(CH$_3$)$_2$C$_{16}$H$_{33}$]$^+$ quaternary ammonium groups.

(B) Cross-linking the polymer chains

Treatment of the quaternized polymer film with a diaminoalkane was then carried out with the aim of cross-linking the polymer chains. In a typical experiment the polymer film that had previously been treated with N,N-dimethylhexadecylamine was treated with a diaminoalkane at elevated temperatures, using the reagent either neat or with added solvent, for reaction times of 2-8 hours. Preferred conditions involve treating the coated membrane with 1,6-diaminohexane in 1,4-dioxane (40 v/v %) at 85 °C for 5 hours.

(C) N-Capping unreacted groups

After cross-linking, treatment of the polymer film with diethanolamine was then carried out at elevated temperature using this reagent either neat or with added solvent, for reaction times of 2-8 hours with the aim of functionalising (capping) the remaining unreacted chloromethyl groups. Preferred conditions involve treating the coated membrane (35 mm) with neat diethanolamine (30 mL) in a conical flask covered with cotton wool at 85 °C for 5 hours.

2.11.12 Rheometer to measure viscosity standard procedures

Viscosity measurements were made using a controlling stress Rheometrics S-5000 rheometer (Rheometrics Instruments, Piscataway, NJ) equipped with a cone and plate geometry. The cone diameter was 20 mm and the cone angle was 4°. All samples of polymer flake (0.20 g) were dissolved in NMP (2.0 mL) and measured for 30-45 min using a steady sweep mode at a temperature of 25 ± 0.1°C.

2.11.13 Method to use analyse samples with Leica DMR research microscope (2 systems)

Two different batchs of polymer were prepared. The first were functionalized smart films with different thicknesses cast onto the backing material. These were monitored directly with a bright-field microscope. The second were the functionalize smart films (100 µm) on backing material that had been immersed in concentrated Orange (II) solution, (0.5 g in 4.0 mL deionised water) and dried under a N$_2$ atmosphere before being examined under fluorescence microscopy (Leica DMR microscope (Oberkochen, Germany)) using Zeiss filter set 2. This Leica DMR microscope (Oberkochen, Germany) equipped with Carl Zeiss Axioplan 2 (DC
500) for bright field, dark field, phase contrast, DIC and fluorescence imaging (100 W mercury arc lamp). They carry a wide range of objective lenses and fluorescence filter cubes. The microscope has a colour camera (1.4-12 mp) and object lenses (1-100x).

2.11.14 Method for use of Andor Revolution spinning disc confocal laser microscopy.

Three different batches of polymer were prepared. The first one was a PCMS polymer produced using the homopolymerization method (no added solvent) with a cast thickness of 50 µm, functionalised by treatment with the N,N-dimethylhexadecylamine, cross-linked by treatment with 1,6-diaminohexane and endcapped with diethanolamine as described in 2.11.11. The film was then immersed in Orange (II) dye solution (200 µM, 20 mL, (0.01M), pH 9.5). The dye adsorbed onto the film and acted as a fluorescence dye. The second one was PCMS produced using the homopolymerization (solventless) method cast with a total thickness of 250 µm, functionalised as described in section 2.11.11 and then immersed in Orange (II) dye solution (200 µM, 20 mL, (0.01M), pH 9.5). The third sample was a PCMS: styrene (1:1) ratio copolymer produced using homopolymerization (no solvent), cast with a thickness of 50 µm, functionalised as described in section 2.11.11 and immersed in Orange (II) dye solution (200 µM, 20 mL, (0.01M), pH 9.5) which acts as fluorescence dye. All 3 samples were soaked in the Orange (II) solutions overnight before being dried under a N2 atmosphere. These samples was then mounted on a round shape glass plate and measured using an Andor revolution spinning disc confocal laser microscope equipped with 20 planapcor lenses at wavelength range between 3500-4000 nm in both the green and red regions. The images obtained across the depths of the samples were monitored using an Andor Ixon 885 camera. The data obtained was then analyzed using imaging software known as Imaris which mainly functions to view and rendered 3D data sets.

2.11.15 Method to use TEM

The samples were prepared from PCMS produced using the homopolymerization method and cast with a thickness of 250 µm onto a PP backing, functionalised as described in section 2.11.2 and immersed in Orange (II) dye solution, (200 µM, 20 mL, carbonate buffer (0.01M), pH 9.5) overnight before drying under a N2 atmosphere. The cast polymer was cut into segments about 2 mm long using a glass knife before being embedded in a capsule containing medium LR gold or LR white resin (London Resin Co.,Ltd, Basingstoke, UK) with 0.1% benzil (w/v) at room temperature on rotator. These segments was immersed in LR gold resin mixture for 1 h before the samples were polymerized at room temperature under UV light. The samples were then cut using a glass knife on an ultramicrotome (model EM UC6 Leica Microsystems, Wetzlar,
Germany) and the segments were transferred onto copper grids and monitored using a Technai FEG20 TEM instrument.

2.11.16 EDX-TEM normal cutting or cutting using a cryo-ultramicrotome

The TEM that was used was a Technai FEG20 (200 kV TEM) instrument that had highly specified STEM and HAADF imaging modes, Gatan energy filter and Edax EDS. In addition, this TEM was equipped with a Gatan Ultrascan 1000, 4 Mpixel digital camera to record conventional and energy filtered images. It also has sample holders including conventional and double tilt room temperature ones, and standard and high tilt cryo holders. In addition, tomography software was also provided.

The sample analysed was a PCMS polymer produced using the homopolymerization method with thickness 250 µm, functionalised by treatment with N,N-dimethylhexadecylamine +1,4-dioxane, 1,6-diaminohexane + 1,4-dioxane and neat diethanolamine. This sample was divided into 2 batches. The first one was immersed in FeB* solution (4.0 mM, 20 mL, carbonate buffer (0.01M), pH 9.5) overnight while another batch was immersed in ammonium molybdate solution (4 mM, 20 mL, carbonate buffer (0.01M), pH 9.5) overnight before drying under a N₂ atmosphere. Next the samples were cut into segments about 2 mm long using a glass knife before being embedded in a capsule containing medium LR gold acrylic (London Resin Co.Ltd, Basingstoke, UK) with 0.1% benzil (v/v) at room temperature on rotator. The sample was left to sit in resin mixture for 1 h before the samples were polymerized at room temperature under UV light. The samples were then cut using a glass knife on an ultramicrotome (model EM UC6 Leica Microsystems, Wetzlar, Germany) before the segments were transferred onto a Cu/Al grid and monitored using the Technai FEG20 TEM instrument. For attempts to produce thin sections using the cryo-ultramicrotome, the naked membrane samples were immersed in liquid nitrogen before being cut, but no sections suitable for analysis were obtained.

2.11.17 Method of sample preparation for SEM studies

Procedure to use SEM start with samples preparation of PCMS polymer produced using homopolymerization method (section 2.11.2) with thickness 250 µm, (functionalised by treatment with N,N-dimethylhexadecylamine +1,4-dioxane, 1,6-diaminohexane + 1,4-dioxane and neat diethanolamine). The sample was then divided into 3 batches. The first one was immersed in FeB* solution in carbonate buffer (4mM, 20 mL, carbonate buffer (0.01M), pH 9.5) overnight. The second one was immersed in ammonium molybdate in carbonate buffer solution change (4.0 mM, 20 mL, carbonate buffer (0.01M), pH 9.5) overnight, while the third
one was immersed in Orange (II) carbonate buffer solution (4mM, 20mL, carbonate buffer (0.01M), pH 9.5) change as before drying under a N₂ atmosphere. The dry samples was then cut into squares about 2 mm in size and mounted on an SEM holder before measurements were made using an SU800 series UHR Cold- Emission Fe-SEM.
CHAPTER 3
3.1 Chapter 3 summary

In this chapter the detailed bleaching experiments that were carried out using 3 different systems, a beaker, a U-tube glass apparatus and finally a cross flow apparatus are discussed. For each system a number of different parameters were investigated to get a better understanding of the heterogeneous system. These included the smart film thickness, types of catalyst, types of dyes, catalyst loading, different pH, concentration of hydrogen peroxide and types of buffer. All the bleaching reactions were monitored using an Ocean Optics UV-vis spectrophotometer at constant ambient temperature 20°C.
3.2 Catalytic oxidation reactions in a Beaker

This system was used for initial oxidation experiments with the smart catalytic film because it was very simple and easy to obtain results and because it enabled the performance of an inorganic catalyst anchored onto the smart film to be investigated in a situation where the hydrogen peroxide solution was not separated from the substrate solution. The idea of initially using this system was to learn more about the nature of the anchored catalyst and its ability to oxidise substrates under the most favourable conditions. Changes to the following parameters were investigated for the catalysts in this configuration were:

- Backing membranes
- Film thickness
- Catalyst loadings of FeB*/FeB^j
- Dyes with different charges
- Type of catalysts
- pH
- Stirring rates
- Different buffer systems
- Different concentrations of hydrogen peroxide

Before the bleaching experiments were investigated in detail the best solid support (or backing) on which to anchor the catalyst had to be chosen. There are a range of commercially available solid support materials such as NF, NF 270, MPF 36 and backing membrane polypropylene backings such as PP 2471 nd and polyester backings. It was decided that most of the detailed studies would be carried out using the PP 2471 nd backing material for supporting the smart catalytic films that would be produced because it was anticipated that this would be the most inert material towards hydrogen peroxide solution.
A schematic diagram of how the synthesised smart films were suspended in the experiments carried out in the beaker oxidation system is shown in Figure 112:

Before the oxidation experiments were carried out, a standard calibration curve of [(FeB*)] vs. initial rate of orange (II) oxidation under standard conditions (pH 9.5, [hydrogen peroxide] 1.00 mM) was obtained. The purpose of this calibration curve was to enable measurements to be made of free catalyst in solution.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>1.0 mM</td>
</tr>
<tr>
<td>Carbonate buffer</td>
<td>pH 9.5, (0.01 M)</td>
</tr>
<tr>
<td>Orange (II) dye</td>
<td>50.0 µM</td>
</tr>
<tr>
<td>FeB*</td>
<td>(0.1, 0.2, 0.5, 1.0, 2.0, 5.0)µM</td>
</tr>
</tbody>
</table>

Table 22: Conditions for the calibration curve of FeB* vs. initial rates of orange (II) oxidation
As the concentration of FeB* was increased, the initial rates of oxidation increased in a linear fashion as had been observed in previous studies of this catalyst. The lowest concentration measured was 0.1 µM because it was expected to be close to a reasonable lower value for the concentration of (FeB*) that might be obtained and still be easily measured in the oxidation studies. The highest concentration of the calibration curve was set at 5 µM. Next a calibration curve with different concentrations of H$_2$O$_2$ was obtained. The conditions used to create this calibration curve are shown in Table 23:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>(0.1,0.25,0.5,0.75,1.0) mM</td>
</tr>
<tr>
<td>Carbonate buffer</td>
<td>pH 9.5,(0.01 M)</td>
</tr>
<tr>
<td>Orange(II) dye</td>
<td>50.0 µM</td>
</tr>
<tr>
<td>FeB*</td>
<td>1.0 µM</td>
</tr>
</tbody>
</table>

Table 23: Conditions for the calibration curve of different [H$_2$O$_2$] vs. initial rates of orange (II) oxidation
Figure 114: Plot of initial rate of Orange (II) dye with different $[\text{H}_2\text{O}_2]$ mM at pH 9.5

(Estimated errors in initial rates ± 5%)

Discussion

As the concentration of hydrogen peroxide increased slowly from 0.1 mM to 0.5 mM, the initial rate of oxidation also increased approximately in a non-linear fashion, again as expected. The corresponding calibration curves were also obtained for the different Fe-TAML catalyst, FeBJ, which was used in some of the experiments described below. The conditions for the calibration curve for FeBJ at pH 9.5 are shown in Table 24:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>1.0 mM</td>
</tr>
<tr>
<td>Carbonate Buffer</td>
<td>pH 9.5, (0.01M)</td>
</tr>
<tr>
<td>Orange (II) dye</td>
<td>50.0 µM</td>
</tr>
<tr>
<td>FeBJ</td>
<td>(0.1,0.2,0.5,1.0,2.0,5.0)µM</td>
</tr>
</tbody>
</table>

Table 24: Conditions for the calibration curve of the initial rate of Orange (II) oxidation vs. FeBJ at pH 9.5.
A similar calibration curve was prepared for FeB$^J$ this time at pH 11 using the conditions in Table 25.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>1.0 mM</td>
</tr>
<tr>
<td>Carbonate Buffer</td>
<td>pH 11, (0.01M)</td>
</tr>
<tr>
<td>Orange (II) dye</td>
<td>50.0 µM</td>
</tr>
<tr>
<td>FeB$^J$</td>
<td>(0.1,0.2,0.5,1.0,2.0,5.0) µM</td>
</tr>
</tbody>
</table>

Table 25: Conditions for the calibration curve of the initial rate of Orange (II) oxidation vs. FeB$^J$ at pH 11.0.
Once these four calibration curves were established, blank experiments needed to be performed to further understand the behaviour of this system under specific conditions. For this Fe-TAML catalyst the calibration curves were all linear, again as previously. Once these four calibration curves were obtained, blank experiments were performed to further understand the behaviour of this system under specific conditions. These blank experiments were obviously necessary to eliminate any possibility that the bleaching observed in the experiments were caused by something else other than the anchored catalyst. The first blank obtained for the beaker system aimed to investigate the effect of having only hydrogen peroxide with Orange (II) dye in a buffer at pH 9.5 but with no catalyst anchored on the film. The conditions are given in Table 26 and the results in Figure 117.

### Conditions

<table>
<thead>
<tr>
<th>[Orange (II)]</th>
<th>[H₂O₂]</th>
<th>Total volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 μM</td>
<td>1.0 mM</td>
<td>20 mL</td>
</tr>
</tbody>
</table>

Table 26: Condition for first blank reaction

(Estimated errors in initial rates ± 5%)

Figure 116: Plot of Initial rate of Orange (II) dye with different [FeB³⁺] μM at pH 11.0
Figure 117: Plot of absorbance of Orange (II) dye with \([H_2O_2]\) µM at pH 9.5

(Estimated errors ± 5%)  

The initial absorbance of Orange (II) was approximately 1. Over the 6 hour time interval, the Orange (II) was slowly bleached to an absorbance of approximately 0.9 by the hydrogen peroxide under these conditions. The absorbance dropped relatively fast to 0.9 over the first 80 minutes and dropped very little after this time. The absorbance then dropped very little over the remaining 320 minutes. Next, the second blank was run to determine the effect of having a smart catalytic film with the catalysts (FeB*) incorporated into it (circular shape 35 mm diameter) and Orange (II) dye in a buffer solution at pH 9.5 but without any hydrogen peroxide present. The conditions are given in Table 27 and the results in Figure 118.

**Conditions**

<table>
<thead>
<tr>
<th>[Orange (II)]</th>
<th>Total volume</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µM</td>
<td>20 mL</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 27: Condition for second blank reaction
Over the 6 hour period, the absorbance of the dye dropped from 1.0 to 0.2. The SCF also took on a pale orange colour during this time, suggesting that the dye was being slowly adsorbed onto the film over this extended period. Presumably an electrostatic attraction between the negatively charged dye and the positively charged quaternary ammonium groups within the polymer was responsible for the adsorption of the dye onto the film. Nevertheless, since typical bleaching experiments were completed in less than 30 min, this blank was repeated again over a 70 minute period and the results are shown below in Figure 119:

![Absorbance vs time for blank experiment with smart catalytic films and FeB* and Orange (II) dye solution](image1)

Figure 118: Plot of absorbance of Orange (II) dye with FeB* anchored on SCF without hydrogen peroxide at pH 9.5

![Absorbance vs time for Orange (II) dye with smart catalytic films and H₂O₂](image2)

Figure 119: Plot of absorbance of Orange (II) dye with FeB* anchored on SCF at pH 9.5
The absorbance was observed to only drop from 1.0 to 0.9 over 30 minutes and to 0.8 over 70 minutes. Therefore, again the drop in absorbance of the dye solution due to dye being adsorbed onto the SCF rather than being oxidised was relatively small over the period of the oxidation experiments.

To confirm that it was the quaternary ammonium groups that were primarily responsible for adsorption of small amounts of the dye onto the polymer, a third blank experiment was conducted to see the effect of hydrogen peroxide on the Orange (II) dye in a buffer solution at pH 9.5 in the presence of a non-functionalised polymer film. The absorbance was monitored over 5.5 hour interval. The conditions are given in Table 28 and the results in Figure 120.

**Conditions**

<table>
<thead>
<tr>
<th>[Orange (II)]</th>
<th>[H₂O₂]</th>
<th>Total volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µM</td>
<td>1.0 mM</td>
<td>20 mL</td>
</tr>
</tbody>
</table>

Table 28: Condition for third blank reaction

![Absorbance vs time for Orange (II) in buffer solution with SF](image)

Figure 120: Plot of absorbance of Orange (II) dye with FeB⁺ anchored on non-functionalised film at pH 9.5

This result shows that a non-functionalised polymer membrane has a very much reduced ability to adsorb the Orange (II) dye as in this case the absorbance dropped from 1.0 to approximately 0.96 over 70 minutes and was still greater than 0.9 after 300 minutes.

It was anticipated that one potential problem that could occur with the smart catalytic film during oxidation experiments was that the catalyst anchored on the film might slowly leach into solution, especially in the presence of the buffer solution. Therefore a set of experiments was
performed to measure the amount of FeB* that leached into solution when the SCF was immersed in buffer solution. The experiments were carried out by taking a functionalised membrane film and immersing it in a buffer solution (carbonate buffer, 0.01 M, pH 9.5) containing FeB* (20 mL, 50 µM) overnight. The membrane was then removed, washed with deionised water and immersed in a freshly prepared carbonate buffer solution (0.01 M) and stirred for 15-20 minutes. This was repeated two more times. Standard bleaching experiments were then carried out (after the addition of appropriate amounts of hydrogen peroxide and Orange (II) dye) using the solution remaining after the smart film had been immersed overnight to initially adsorb the FeB* (bleaching run 1, Table 30) and the three carbonate buffer solutions in which the film had been immersed for 15-20 minutes (runs 2-4, Table 30). The results are summarised in Table 30:

**Conditions**

<table>
<thead>
<tr>
<th>[Orange (II)]</th>
<th>[H₂O₂]</th>
<th>Total volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µM</td>
<td>1.0 mM</td>
<td>20 mL</td>
</tr>
</tbody>
</table>

*Table 29: Condition to measure leaching reaction*

**Result**

<table>
<thead>
<tr>
<th>Bleaching run</th>
<th>Initial rate (mol L⁻¹ s⁻¹)</th>
<th>FeB* leached from film (µ mol L⁻¹)</th>
<th>Moles of FeB* leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.414 x 10⁻⁷</td>
<td>2.938</td>
<td>0.059 µmole</td>
</tr>
<tr>
<td>2</td>
<td>5.015 x 10⁻⁷</td>
<td>1.472</td>
<td>0.029 µmole</td>
</tr>
<tr>
<td>3</td>
<td>1.747 x10⁻⁷</td>
<td>0.382</td>
<td>0.008 µmole</td>
</tr>
<tr>
<td>4</td>
<td>Not measurable</td>
<td>Not measurable</td>
<td>Not measurable</td>
</tr>
</tbody>
</table>

*Table 30: Summary bleaching reaction*

These results show that of the total 1.0 µmoles of FeB* in the original solution, 0.059 µmole was not adsorbed onto the film and remained in solution (run 1). Furthermore, in total only 0.9042 µmole of the FeB* that was adsorbed onto the film leached into the three buffer solutions during the successive immersion steps. Clearly the majority of the adsorbed FeB* remains tightly adsorbed onto the film. On the basis of these results, all smart catalytic films produced were immersed in buffer solution three times for 20 minutes after the FeB* was adsorbed onto the film.
Although these experiments indicated that very little FeB* indeed leached from the film into buffer solution after treatment with the buffer solutions, it was still possible that detectable amounts of FeB* would leach into solution during actual bleaching runs where dye and hydrogen peroxide were present in the buffer solution. To test this possibility, a bleaching experiment in the presence of the SCF was carried out, but the film was removed from solution after approximately 1/3 of the dye had been bleached. The absorbance of the solution was then monitored for a set time after which the SCF was returned back into the same solution and the oxidation reaction resumed. If FeB* had been leached into the solution, this would have caused bleaching of the dye at a measurable rate during the period the SCF was not present in the solution. The absorbance vs time plot of the solution was measured under the conditions in Table 31 and the results are presented in Figure 121.

**Conditions**

<table>
<thead>
<tr>
<th>Orange (II)</th>
<th>FeB*</th>
<th>[H₂O₂]</th>
<th>Total volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 µmole</td>
<td>1.0 µmole</td>
<td>1.0 mM</td>
<td>20 mL</td>
</tr>
</tbody>
</table>

Table 31: Condition to measure leaching of catalyst

**Result**

![Absorbance vs time for bleaching Orange (II) solution (pH 9.5). SCF removed from solution at 4 minute, and returned at 10 minute.](image)

Figure 121: Plot of Absorbance vs time for bleaching of Orange (II). SCF removed from solution at 4 minute and returned at 10 minute.

This result clearly shows that when the SCF was removed, the bleaching did not continue. It was only after it was placed back into the solution that the bleaching continued to completion. In further experiments the catalase activity of the FeB* anchored on the film was investigated. The film was inserted into a buffer solution containing hydrogen peroxide, but no dye.
Hydrogen peroxide test strips were used to check concentration of peroxide remaining in solution after set times. In addition, attempts were made to find conditions under which all the FeB* would be degraded by treatment with large amounts of hydrogen peroxide in buffer solution.

### Conditions

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$ (35 ppm)</td>
<td>20.0</td>
<td>2.0 x 10$^{-5}$</td>
</tr>
<tr>
<td>(FeB*)</td>
<td>20.0</td>
<td>1.0 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

Table 32: Condition to measure catalase activity of the FeB*

Under the conditions in Table 32, the concentration of hydrogen peroxide dropped from 30 mg/L (1.0 mM H$_2$O$_2$) to approximately 1 mg/L (0.033 mM H$_2$O$_2$) in 1.5 hours. Even after 6 hours, the [H$_2$O$_2$] concentration continued to slowly decrease over time. Hence the assumption was made that it takes at least 12 hours to overnight for the reaction to completely degrade the FeB*.

### 3.2.1 Thickness of the SCFs

Another parameter that was investigated before extensive oxidation experiments with the SCFs were carried out was the thickness of SCF. Initially films were generated with a nominal thickness of 50 - 100 µm. The term nominal thickness here means the thickness of the cast film (or films in the case of casting multiple coats of polymer), not the thickness of the final cured and functionalised film. It was not possible to measure the thickness of the final SCFs because the polymer penetrated the backing, thereby preventing any meaningful measurements from being made. Since it was discovered that films of 50 - 100 µm nominal thickness often had pinholes (see Chapter 2) most of the films discussed below were generated by casting and curing five separate polymer films each of nominal thickness of 50 µm to give a final film of 250 µm nominal thickness.
3.2.2 Oxidation experiments carried out in beakers

The following experiments were done to investigate the effect of bleaching at pH 7, at a stirring speed of 750 rpm using the (FeB*) catalyst and the PCMS+NMP membrane (250 µm nominal thickness) at different catalyst loadings (mole ratio of catalyst: dye) ranging from (1:1) ratio to (80:1) ratio. Other parameters are the same as those used in section 3.2

This result shows that as the catalyst loading increased, the initial rate of oxidation also increased. From a catalyst: dye ratio above 40:1, the rate did not increase with increasing amounts of catalyst adsorbed onto the film. This indicates that after this point the rate determining step (RDS) is no longer the rate at which the immobilised catalyst oxidises the dye, but instead another step in the oxidation process has become rate determining. It is proposed that the new RDS under these circumstances is the transport of the Orange (II) dye to the active catalyst sites.

Figure 122: Plot of initial rate of oxidation vs catalyst (FeB*) to dye mole ratio at pH 7
Once it was confirmed that the reaction occurred at pH 7, it was also important to monitor the rate of reaction at pH 9.5 since in a homogeneous system at pH 9.5, the initial rate obtained for an FeB* concentration of 1 µmol L\(^{-1}\) (2x 10\(^{-7}\) mol L\(^{-1}\) s\(^{-1}\)) which is much faster than the rate at pH 7 (0.1 x 10\(^{-7}\) mol L\(^{-1}\) s\(^{-1}\)). Experiments were conducted using a 250 µm thickness PCMS + NMP SCF, at pH 9.5 while the rest of the variables were the same as those used in 3.2.2 The FeB* catalyst : dye ratios ranged from (1:1) to (140:1).

The result are plotted in Figure 123

![Figure 123: Plot of initial rate of Orange (II) oxidation vs catalyst (FeB*) to dye mole ratio at pH 9.5](image)

These results show that as the catalyst loading ratio increased, the initial rate of oxidation also increased but as the catalyst: dye ratio approached approximately 60:1, the initial rate reached a plateau which meant any further increase of the amount of the catalyst after this point essentially did not increase the initial rate further. Again, it is proposed that the rate-limiting step under these circumstances becomes the transport of the Orange (II) dye to the active catalyst sites. This is similar to what was observed at pH 7.0, although the rates of oxidation are approximately 10 times faster at this pH.

Next, a series of consecutive catalytic oxidation reactions were performed using a PCMS + NMP SCF (100 µm nominal thickness) under the conditions shown in Table 33. Complete bleaching occurred within 12 minutes for the first oxidation reaction and remarkably when the bleaching reaction was repeated 10 times using the same smart catalytic film without the addition of any extra catalyst, the time taken for complete bleaching remained the same. The
results are presented in Figure 124. This repeated bleaching was done to determine how well the catalyst survived when carrying out oxidation reactions over an extended period of time. In this particular case the catalyst appeared to survive remarkably well.

<table>
<thead>
<tr>
<th>Orange (II)</th>
<th>FeB*</th>
<th>H$_2$O$_2$</th>
<th>[Carbonate buffer]</th>
<th>Stirring speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 µmole</td>
<td>1.0 µmole</td>
<td>20.0 µmole</td>
<td>0.010 M</td>
<td>150 rpm</td>
</tr>
</tbody>
</table>

Table 33: Conditions to measure bleaching activity of FeB*

![Absorbance vs time for PCMS +NMP (5h) 10 times bleaching](image)

Figure 124: Bleaching of Orange (II) using PCMS +NMP SCF

(Estimated error ± 5%)
This same multiple bleaching experiment was carried out using two further SCFs (Copolymer + (0.5%) DVB and PCMS + (0.5%) DVB) and the results are presented in Figures 125 and 126. Although in both of these cases the time to achieve complete bleaching for the first few bleaching runs was also approximately 12 minutes, some catalyst degradation clearly occurred because the time for complete bleaching increased to more than 20 minutes by the time the 10th bleaching run was carried out. Clearly the smart catalytic films (Copolymer + (0.5%) DVB and (PCMS + (0.5%) DVB) that were cross-linked with DVB did not perform as well under these conditions as the film PCMS + NMP that was cross-linked with 1,6-diaminohexane.

![Absorbance vs time PCMS + (0.5%) DVB at pH 9.5 (1:1) mole ratio](image)

**Figure 125**: Bleaching of Orange (II) using PCMS + (0.5%) DVB SCF

(Estimated error ± 5%)
Once the 3 best smart catalytic films were chosen, the next step was to confirm that there was no leaching thorough out the reaction. This was done by running the reaction with the smart catalytic film but then removing the membrane half-way through the reaction before putting it back into the solution as explained previously (see Figure 121).

Next, it was investigated how long the FeB* catalyst survived after being exposed to hydrogen peroxide in the absence of any substrate to oxidise. When FeB* is exposed to hydrogen peroxide alone in homogeneous solution at pH 9.5 it decomposes with a half-life of about 10-15 minutes. Therefore experiments were conducted to see how well the SCF could still bleach Orange (II) dye after being immersed in hydrogen peroxide for a set period of time at pH 9.5. The results of this experiment should indicate the life time of the catalyst when adsorbed on the film and in the presence of hydrogen peroxide alone.

This experiment was done by re-immersing the SCF (PCMS+NMP with 1.0 µmole FeB* anchored onto it) into a hydrogen peroxide solution (1.0 mM) for a set time and then using the SCF in bleaching runs to measure its activity (the conditions are given in Table 34). The [H₂O₂] concentration present in the solutions after a set time period and before bleaching commenced was monitored using H₂O₂ test strips. At time zero, the initial concentration of H₂O₂ 1.0 mM, or 35 mg/L. After 1.5 hours the concentration had dropped to 3-10 mg/L. The concentration of H₂O₂ was adjusted so that the concentration was returned to 1.0 mM and then a bleaching experiment was carried out. After this first bleaching experiment, the SCF was removed from solution, rinsed with water and then re-immersed in hydrogen peroxide solution for 3.5 hours and then used for a second bleaching experiment. In this way the SCF was exposed to hydrogen peroxide solution for a cumulative total of 16.5 hours before the final bleaching experiment was carried out.

### Condition

<table>
<thead>
<tr>
<th>Orange (II)</th>
<th>FeB*</th>
<th>H₂O₂</th>
<th>[Carbonate buffer]</th>
<th>Stirring speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 µmole</td>
<td>1.0 µmole</td>
<td>1.0 mM</td>
<td>0.010 M</td>
<td>150 rpm</td>
</tr>
</tbody>
</table>

Table 34: Conditions used to measure bleaching activity of the FeB* after exposure to 1.0 mM H₂O₂

The results given in Figure 127 clearly show that the performance of the SCF decreases as the time of exposure to hydrogen peroxide increases. However, even after exposure to hydrogen peroxide for 8 hours in total, in addition to carrying out 4 separate bleaching runs, the SCF was still able to completely bleach orange II solution in less than 50 minutes. Clearly the lifetime of the catalyst in the presence of hydrogen peroxide solution is significant.
of FeB\textsuperscript{*} in the presence of hydrogen peroxide alone is much longer when adsorbed onto the SCF than it is in homogeneous solution.

These same experiments were also carried out at pH 11 for the SCFs PCMS + NMP, PCMS + DVB 0.5\% and Copolymer + DVB 0.5\%. The results obtained are given in Figures 128, 129 and 130. In addition, three best membranes (PCMS+NMP, PCMS +DVB 0.5\% DVB and Copolymer + 0.5\%DVB) were also investigated at pH 11 under the conditions shown in Table 35:

<table>
<thead>
<tr>
<th>Smart film (SF)</th>
<th>FeB\textsuperscript{*}: Orange II mole ratio</th>
<th>H\textsubscript{2}O\textsubscript{2}</th>
<th>[Carbonate buffer]</th>
<th>Stirring speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCMS + NMP</td>
<td>(1:1)</td>
<td>1.0 mM</td>
<td>0.01 M</td>
<td>750 rpm</td>
</tr>
<tr>
<td>PCMS + DVB 0.5%</td>
<td>(1:1)</td>
<td>1.0 mM</td>
<td>0.01 M</td>
<td>750 rpm</td>
</tr>
<tr>
<td>Copolymer + DVB 0.5%</td>
<td>(1:1)</td>
<td>1.0 mM</td>
<td>0.01 M</td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 35: Condition for bleaching reaction at pH 11 for 3 best SCF
Condition for bleaching reaction at pH 11 for 3 best SCF

Figure 127: Bleaching of Orange (II) using PCMS + DVB (0.5%)
(Estimated error ± 5%)

Figure 128: Bleaching of Orange (II) using Copolymer + DVB (0.5%) SCF
(Estimated error ± 5%)
The results show that over the 10 bleaching runs using the PCMS + NMP SCF, the time taken for complete bleaching increased from 50 to 280 seconds, and for both the PCMS + 0.5% DVB and Copolymer + 0.5% DVB SCFs the time for complete bleaching increased from 150 to 330 seconds. This shows that the PCMS + NMP SCF again performed the best among the three smart films tested. The results indicate that at pH 11 the catalyst undergoes much faster decomposition than it does at pH 9.5, possibly because the rate of formation of the active catalytic species is faster which results in the catalyst spending a greater proportion of its time in this activated form where, in the absence of substrate, it decomposes relatively rapidly.

One of the objectives was to generate SCFs that could carry out oxidation reactions as fast as possible. Therefore, it was important to try to determine the rate limiting steps in the overall oxidation reactions. In order to reach this goal, smart films that were of 250 μm nominal thickness were made. As might be expected, it was discovered that increasing the film thickness allowed more catalyst to be loaded onto the membrane. Therefore, bleaching experiments with these films (PCMS +NMP) were carried out to investigate how this changed the reaction rates. This was achieved by using smart films of a circular shape (35 mm) which had a nominal polymer thickness of 250 μm. 140 μmoles of FeB* were adsorbed onto these films and this corresponded to a mole ratio of FeB*catalyst: dye of 140:1 during standard bleaching experiments. Bleaching was investigated at pH 9.5 and pH 11 with a stirring speed of 500-750 rpm (see Figure 131 and 132) under the conditions shown below in Table 36. Once the bleaching was complete, another experiment was carried out in which the SCF was removed.

(Estimated error ± 5%)
during the bleaching experiment for a set time and then returned to confirm that no significant FeB* had leached into the solution (see Figures 133 and 134).

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20 mL</td>
<td>2.0 \times 10^{-5}</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20mL</td>
<td>1.0 \times 10^{-6}</td>
</tr>
<tr>
<td>FeB*</td>
<td>On membrane</td>
<td>1.4 \times 10^{-4}</td>
</tr>
</tbody>
</table>

| Stirring speed | 750 rpm |

Table 36: Bleaching condition for 3 best SCFs at pH 11

Figure 130: Bleaching of 250 µm thickness PCMS +NMP SCF (140:1) mole ratio at pH 9.5

(Estimated error ± 5%)
Figure 131: Bleaching of 250 µm thickness PCMS + NMP SCF (140:1) mole ratio at pH 11.0

(Estimated error ± 5%)

Figure 132: Bleaching of 250 µm thickness PCMS + NMP membrane 250 µm thickness 1 at pH 9.5 removed and returned 2 minutes later

(Estimated error ± 5%)
These results in Figures 133 and 134 show that at most extremely small amounts of catalyst leach out from the SCF, even at this very high loading of catalyst, thus proving that the observed bleaching was caused by the catalyst anchored on the SCF and that the catalyst is strongly adsorbed.

The results show that at pH 11, the dye is oxidised much faster than at pH 9.5 (10-40 seconds vs 180-240 seconds, respectively). This is now in line with the relative rates of oxidation in homogeneous solution and indicates that rather than FeB* undergoing activation by a different mechanism when adsorbed onto the SCF at pH 11, the relatively slow rate of oxidation previously observed at this pH (Figure 132) is probably due to the relatively rapid catalyst decomposition under these conditions. In the present example there is 140 times the amount of catalyst adsorbed and so the effects of catalyst decomposition are not so apparent. In both cases the SCFs undergo 10 bleaching cycles with some loss of activity, but overall the rates of oxidation remain fast. Comparing Figures 130 and 132 shows that for the initial bleaching results at pH 11, the time for complete bleaching decreases from about 40 seconds to 10 seconds as the amount of catalyst on the film increases 140 times. Likewise, the comparison between Figures 124 and 131 shows that for the initial bleaching results at pH 9.5, the time for complete bleaching decreases from about 12 minutes to 4 minutes as the amount of catalyst on the film increases 140 times. Clearly the time taken for complete bleaching does not decrease in direct

![Absorbance vs time for PCMS NMP membrane 250µm thickness at pH 11 removed at time 15 second and returned back at 30 second](image)

Figure 133: Plot to measure leaching of FeB* using 250 µm thickness SCF (140:1) mole ratio, pH 9.50

(Estimated error ± 5%)
proportion to the amount of catalyst present. This suggests that oxidation of the substrate by the catalyst may not be the slow step in the overall oxidation reaction at high catalyst loadings.

Bleaching reactions were also carried out at pH 6.0 to further investigate if the SCF would behave differently compared to a homogenous catalytic system at pH 6.0. The reaction was performed using a PCMS + NMP SCF (100 µm thickness) using condition in Table 37 at pH 6.0 in phosphate buffer (0.01 M). The results are plotted in Figure 135.

Conditions

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20 mL</td>
<td>2.0×10⁻⁵</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20 mL</td>
<td>1.0×10⁻⁶</td>
</tr>
<tr>
<td>(FeB⁺)</td>
<td>On membrane</td>
<td>6.0×10⁻⁵</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 37: Bleaching condition for 3 best SCF at pH 6

Figure 134: Bleaching of 100 µm thickness PCMS +NMP SCF (60:1) mole ratio FeB⁺: Orange (II) dye at pH 6.0

(Estimated error ± 5%)
This result clearly shows that essentially no catalytic bleaching takes place at pH 6.0 which is in line with the results obtained in homogeneous solutions of the catalyst.

Given the results obtained for initial rates of bleaching vs increasing catalyst loadings (see Figure 130-132) attempts were made to determine the factors that might determine the rate of dye oxidation at high catalyst loadings. The first variable that was investigated was the stirring speed to see if rate of delivery of substrate to the SCF influences the rates of the bleaching reactions. These reactions were carried out at pH 9.5 under the conditions stated below in Table 38 using the PCMS + NMP smart film at a 1:1 mole ratio. The results are presented in Figure 136.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>stirring rate</td>
<td>100 rpm, 300 rpm, 550 rpm, 750 rpm and 1000 rpm</td>
<td></td>
</tr>
</tbody>
</table>

Table 38: Bleaching condition for PCMS +NMP SCF with different stirring rate at pH 9.5

Figure 135: Bleaching using PCMS +NMP SCF (1:1) mole ratio pH 9.5 with different stirring speed
(Estimated error ± 5%)
The results show that the stirring speed does play an important role in decreasing the time for the dye to be completely bleached. As the stirring speed was increased from 100 – 750 rpm (using a (0.2 x 0.9) cm Teflon coated magnetic stirring bar) it took less time for complete bleaching. However, increasing the stirring speed to 1000 rpm did not increase the time taken for complete bleaching at all. This indicates that bulk transport of the dye to the surface of the SCF is a rate determining step under these conditions up to a stirring speed of 750 rpm, but that at speeds faster than this there is another step that becomes rate limiting.

The experiments described up to this point have only involved using the dye Orange (II), which is negatively charged in basic solution. Two other dyes were investigated, pinacyanol chloride (PCl) and safranine O. Both these dyes are positively charged whereas Orange (II) is negatively charged in alkaline solution. In homogeneous solution the FeB* catalysed oxidation of PCl is very fast compared to orange (II), whereas the oxidation of safranine O is very slow. By investigating the bleaching of these two dyes in the presence of the SCFs it might be possible to determine the effect that the electrostatic charges have on the rate of catalytic bleaching as well as the relative rates between two dyes with the same positive charge.

A blank run was first performed with pinacyanol chloride in a homogenous solution before proceeding with the bleaching runs in the heterogeneous system using the SCFs. The results are plotted in Figure 137. The dye was bleached very fast and the reaction was finished in less than 1 minute. Condition for experiment simplified in Table 39.

**Conditions**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>Moles</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>20.0</td>
<td>$2.0 \times 10^{-5}$</td>
<td>1.0 mM</td>
</tr>
<tr>
<td>Pinacyanol chloride</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
<td>50.0 µM</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
<td>50.0 µM</td>
</tr>
</tbody>
</table>

Table 39: Bleaching condition for PCMS +NMP SCF (1:1) mole ratio of FeB*: PCl in homogenous system
Using a PCMS + NMP membrane with adsorbed FeB*, a series of ten consecutive bleaching runs were performed under the conditions listed in Table 40. The results are given in Figure 138.

![Absorbance vs time for PCMS +NMP membrane (100 μm), (1:1) mole ratio FeB*: pinacyanol chloride dye at pH 9.5 (λmax 600 nm)](image)

**Figure 136: Bleaching (1:1) mole ratio of FeB*: PCI at pH 9.5 in homogeneous system**

Using a PCMS + NMP membrane with adsorbed FeB*, a series of ten consecutive bleaching runs were performed under the conditions listed in Table 40. The results are given in Figure 138.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻³</td>
</tr>
<tr>
<td>Pinacyanol chloride</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>FeB*</td>
<td>On SCF</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Stirring rate</td>
<td></td>
<td>500-750 rpm</td>
</tr>
</tbody>
</table>

**Table 40: Condition of bleaching using PCMS+NMP (1:1) mole ratio with PCI at pH 9.5**
In an attempt to speed up the bleaching experiments, the amount of FeB* adsorbed onto the SCF was increased by 10 fold and another bleaching experiment attempted using the same conditions listed in Table 41 but with 20 µmole FeB* anchored onto the SCF. However, in this case the reaction took place so quickly accurate absorbance measurements could not be obtained. Further oxidation reactions with PCl were therefore not pursued further.

Attention was then turned to the bleaching of safranine O. Again a reaction for comparative purposes was carried out in homogenous solution before proceeding with the bleaching runs with the SCFs in heterogeneous systems. This reaction was carried out using the conditions listed in Table 41:

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>3.0</td>
<td>( 3.0 \times 10^{-6} )</td>
</tr>
<tr>
<td>safranine O</td>
<td>20.0</td>
<td>( 1.0 \times 10^{-6} )</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>( 1.0 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

Table 41: Condition of bleaching using (1:1) mole ratio FeB*: safranine O at pH 11

(Figure 137: Bleaching of 250 µm thickness PCMS +NMP (1:1) mole ratio of FeB*: PCl at pH 9.5 (Estimated error ± 5%))
Attention was then turned to oxidation reactions of this dye using SCFs. With a PCMS + NMP SCF using the conditions listed in Table 42 (anchored on smart film), a bleaching run was performed at pH 9.5 and the results are plotted in Figure 140. The rate of bleaching under these conditions was very slow and after 3 hours the absorbance had only dropped to 0.8.

Figure 138: Plot of bleaching for PCMS+NMP SCF (1:1) mole ratio at pH 11.0

Figure 139: Plot bleaching of PCMS +NMP SCF using safranine O, (1:1) mole ratio pH 9.5
To speed up the bleaching rate, the number of moles of FeB* on the SCF was increased by a factor of 10. The rest of the variables remained the same. Ten consecutive bleaching runs were performed using this one SCF and the results are given in Figure 141. After the 10th bleaching run, a further bleaching experiment was carried out in which the SCF was removed from solution part way through the bleaching experiment and then returned to determine if any FeB* had leached from the membrane into the solution. The results are displayed in Figure 142.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>safranine O</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>1.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Stirring rate</td>
<td>500 rpm</td>
<td></td>
</tr>
</tbody>
</table>

Table 42: Condition of bleaching using PCMS+NMP SCF (10:1) mole ratio with safranine O at pH 9.5

![Absorbance vs time for safranine O, 518 nm for PCMS +NMP membrane 10:1 mole ratio FeB*: safranine O, 100 µm thickness](image)

**Figure 140:** Bleaching of PCMS +NMP SCF for safranine O (10:1) mole ratio, 100 µm thickness, pH 9.5

**Figure 141:** Bleaching for PCMS +NMP SCF (10:1) mole ratio pH 9.5 removed at 4 minute and returned back at 10 minute
The results in Figure 1 show that complete bleaching occurred relatively quickly under these conditions and there was only a small increase in time taken for complete bleaching between the first and tenth cycle (time increasing from approximately 12 to 16 minutes). It is noteworthy that under the same conditions an orange II solution was fully bleached in (10-16) minutes. In comparison, under homogeneous conditions catalytic bleaching of orange II 10 times faster than safranine O. The results displayed in Figure 142 show that essentially no free FeB* leaches from the SCF during these oxidation reactions.

Bleaching experiments involving safranine O with SCFs loaded with much higher amounts of FeB* were also investigated. Solutions at two different pH values were used in this process. The first bleaching was done at pH 9.5 while another separate bleaching was conducted at pH 11. The conditions are summarised in Table 43 and the results are displayed in Figures 143 and 144. Once the bleaching had finished, another experiment was carried out that involved removing the SCF part way through the reaction to confirm that no significant FeB* had leached back into the solution (see Figure 145).

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>20.0</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>safranine O</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>500-750 rpm</td>
</tr>
</tbody>
</table>

Table 43: Condition of bleaching using PCMS+NMP SCF (140:1) mole ratio with safranine O at pH 9.5
Figure 143: Bleaching for PCMS +NMP SCF (140:1) mole ratio in beaker with safranine O pH 9.5
(Estimated error ± 5%)

Figure 144: Bleaching for PCMS +NMP SCF (140:1) mole ratio in beaker with safranine O pH 11.0
(Estimated error ± 5%)
The results show that at pH 9.5 complete bleaching of safranine O occurred after about 16-29 minutes while at pH 11.0, the bleaching completed after about 7-10 minutes. In comparison, orange (II) was completely bleached in about 4-5 minutes at pH 9.5 and between 10-40 seconds under identical conditions (see Figure 131-132). By way of comparison, in homogeneous solution orange (II) is typically bleached about 10 times faster than safranine O. The reduced difference again suggests that processes other than the chemical oxidation step involving the dye and the activated catalyst contribute to the overall rate of these oxidation reactions. The results in Figure 145 show that essentially no FeB* was leached from the SCF in these reactions.

In an attempt to increase the life time of the catalyst on these smart films, experiments were carried out using lower concentrations of H$_2$O$_2$ since it is well documented that in homogeneous solution treatment of FeB* with hydrogen peroxide alone fairly rapidly leads to catalyst destruction. Three consecutive bleaching reactions of orange (II) were carried out at pH 11 using the conditions detailed in Table 44:

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>20.0</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>$8.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>stirring speed</td>
<td>20.0</td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 44: Condition of bleaching using PCMS+NMP SCF (80:1) mole ratio with Orange (II) at pH 11
This results obtained are presented in Figure 146. The first experiment took about 12 seconds for complete bleaching to occur. This compares with about 10 seconds for a similar experiment with almost twice the amount of FeB* present on the SCF (see Figure 132). There is a similar amount of spread in the bleaching times to those in Figure 132. However, the results show that bleaching still occurs at essentially the same rate, even though the hydrogen peroxide concentration had been decreased tenfold and there is half the amount of catalyst present.

The same reaction with reduced hydrogen peroxide concentration was repeated but with the reaction taking place at pH 9.5. The conditions are listed in Table 45 and the results of the five consecutive runs are given in Figure 147. The times for complete bleaching are slower, but again are similar to the results obtained with twice the amount of catalyst present and ten times the concentration of hydrogen peroxide (see Figure 131).

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O_2</td>
<td>20.0</td>
<td>2.0 \times 10^{-6}</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>1.0 \times 10^{-6}</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>8.0 \times 10^{-5}</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 45: Condition of bleaching using PCMS+NMP SCF (80:1) mole ratio with Orange (II) at pH 9.5.
In view of these interesting results, the concentration of $\text{H}_2\text{O}_2$ was lowered further to 0.01 mM. The concentration of the Orange (II) was 50 µM, the pH was 9.5 and the stirring rate was 750 rpm as before. At this concentration, the number of moles of hydrogen peroxide present was approximately one fifth of the number of moles of dye. The conditions are tabulated in Table 46 and the results are given in Figure 148.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>20.0</td>
<td>$0.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>$8.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 46: Condition of bleaching using PCMS+NMP (80:1) mole ratio with Orange (II) at pH 9.5 with 0.01 mM $\text{H}_2\text{O}_2$. 

Figure 147: Bleaching for PCMS+NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange (II), 0.1 mM $\text{H}_2\text{O}_2$. 

Figure 148: Plot of Absorbance vs time for (80:1) ratio, pH 9.5, in beaker 750 rpm, 0.1 mM $[\text{H}_2\text{O}_2]$.
Surprisingly, the absorbance of the solution dropped about 20% to 0.8 over 9 minutes, suggesting that the catalyst utilised the hydrogen peroxide quite efficiently, but there was insufficient peroxide for complete oxidation. It took close to 9 minutes to reach the 0.8 value and this suggests that the rate of oxidation was considerably slower with this much lower concentration of hydrogen peroxide.

In an attempt to learn more about the stability of the oxidised catalyst specied adsorbed on the membrane, a SCF containing 1.0 µmole of FeB* was immersed in 0.10 mM hydrogen peroxide solution (20 mL, 0.01 M carbonate buffered at pH 9.5) and stirred it for 10 minutes. It was then removed and washed with deionised water for 10-15 minutes. The SCF was then placed into an Orange (II) dye solution (50 µM, 20 mL) in carbonate buffer at pH 9.5. A plot of the absorbance against time obtained is depicted in Figure 149. The orange II solution was bleached completely in about 15 minutes. This is slower than the approximately 4 minutes it took for an equivalent reaction that was carried out in the presence of an excess of hydrogen peroxide (See Figure 131). Nevertheless it is very important in showing that the oxidised catalyst remains active for tens minutes in the SCF.
The SCF from this experiment was then used in the same way for three additional bleaching cycles in which it was treated with hydrogen peroxide (1.0 mM), washed and then added to an orange II solution under the same conditions. The results are presented in Figure 150. It can be seen that the catalyst finally appears to be significantly decomposing after the third cycle as the time for complete bleaching increases significantly at this point.

Figure 149: Bleaching for PCMS +NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange II (Estimated error ± 5%)

Figure 150: Bleaching for PCMS +NMP SCF (80:1) mole ratio pH 9.5 in beaker with Orange (II), exposed to 1.0 mM H_2O_2
Once it was proven that pH, catalyst loading, H\textsubscript{2}O\textsubscript{2} concentration, stirring rate and the nature of the dyes can all play a role in determining the overall rate of the oxidation reactions, the use of different types of oxidation catalysts on the SCFs was investigated to confirm that SCFs can successfully operate with catalysts other than FeB\textsuperscript{*}. Experiments were therefore carried out using the Fe-TAML FeB\textsuperscript{I} (C\textsubscript{16}H\textsubscript{16}ClFeK\textsubscript{2}Na\textsubscript{4}O\textsubscript{4}), ammonium molybdate or sodium tungstate adsorbed on the SCFs.

In the first instance FeB\textsuperscript{I} was used at pH 7 and under the same conditions as the FeB\textsuperscript{*} experiments so that the two results could be compared.

![Initial rate vs catalyst loading for FeB\textsuperscript{I} pH 7.0](image)

**Figure 151: Plot of initial rate of oxidation vs catalyst to dye mole ratio FeB\textsuperscript{I} pH 7**

(Estimated error ± 5%)

Overall at this pH, the initial rates of the dye oxidation by FeB\textsuperscript{I} on the SCF were similar to those of equivalent amounts of FeB\textsuperscript{*} (see Figure 122).

Next, some oxidation reactions were carried out at pH 9.5 as this is the pH at which FeB\textsuperscript{I} catalyses oxidations with hydrogen peroxide the most rapidly\textsuperscript{219}. Experiments were carried with different catalyst loadings of (FeB\textsuperscript{I}) on the SCF at this pH using a membrane that was 250 µm thick. The remaining conditions for these experiments are summarised in Table 48. The catalyst loading ranged from 1.0 × 10\textsuperscript{-6} moles which corresponds to a catalyst to dye ratio of
1:1, through to $1.0 \times 10^{-4}$ moles (catalyst: dye mole ratio 100:1). This would enable a direct comparison to be made with the performance of the (FeB*) catalyst. The results are presented in Figure 152.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>20.0</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>FeB$^+$</td>
<td>20.0</td>
<td>Range from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 47: Condition of bleaching using PCMS+NMP SCF mole ratio (1:1) to (100:1) with FeB$^+$: Orange (II) at pH 9.5 with 1.0 mM H$_2$O$_2$.

The result are plotted below:

![Figure 152: Plot of initial rate of oxidation vs catalyst loading for FeB$^+$ and FeB* at pH 9.5](image)

This result shows that as the catalyst loading increased, the initial rate of oxidation also increased but as the catalyst loading approached a catalyst: dye mole ratio of 20:1, the plot started to plateau. Increases in the amount of catalyst present on the SCF after this point did not increase the initial rate any further. Presumably the rate limiting step after this point becomes the transport of the dye to the oxidation sites.
On comparing both catalysts, the initial rate of oxidation using (FeB\textsuperscript{J}) was found to be faster than that of FeB\textsuperscript{*} at pH 9.5 (8 \times 10^{-6} vs 6.5 \times 10^{-6} mol L\textsuperscript{-1} s\textsuperscript{-1}) for a catalyst loading up to 20 \mu moles (i.e. catalyst: dye mole ratio 20:1) but slower than FeB\textsuperscript{*} for catalyst loadings of 70 \mu moles (i.e. 70:1 mole ratio) and above where the rate of oxidation by the FeB\textsuperscript{*} catalyst on the SCF plateaued at 1.2 \times 10^{-5} L mol\textsuperscript{-1} s\textsuperscript{-1}.

In addition, comparisons of the bleaching reactions with FeB\textsuperscript{J} were also carried out using the three selected membranes; PCMS + NMP, PCMS + 0.5% DVB and Copolymer +0.5% DVB with 1.0 \mu mole of adsorbed catalyst (catalyst:dye mole ratio 1:1) at pH 9.5. This was done to compare the performance of SCFs (100 \mu m thick on polypropylene backing material) with this catalyst. Ten consecutive experiments were carried out with each SCF to determine if the catalyst remained functional when exposed to repeated bleaching reactions. The conditions for the bleaching experiments are given in Table 49 and the results are presented in Figure 153-155.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>20.0</td>
<td>2.0 \times 10^{-5}</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>1.0 \times 10^{-6}</td>
</tr>
<tr>
<td>FeB\textsuperscript{J}</td>
<td>On membrane</td>
<td>1.0 \times 10^{-6}</td>
</tr>
</tbody>
</table>

Table 48: Condition of bleaching using PCMS+NMP mole ratio (1:1) with FeB\textsuperscript{J}; Orange (II) at pH 9.5 with 1mM H\textsubscript{2}O\textsubscript{2}.

In a separate set of experiments, a bleaching run was carried out using new samples of each of the three SCFs (PCMS+ NMP, PCMS+ 0.5% DVB and Copolymer +0.5% DVB) using same conditions listed in Table 48. However, in this case the SCFs were immersed in hydrogen peroxide solution for one hour before the bleaching runs were performed. Three consecutive bleaching runs were carried out in this way for each SCF. The results are given in Figures 156 – 158. Even after immersion in hydrogen peroxide solution for a total of 3 hours and then performing three bleaching runs the catalyst was still performing with only slightly reduced activity in all cases. These remarkable results show that the catalyst FeB\textsuperscript{J} also shows a much increased lifetime when anchored onto the SCFs since the half-life of this catalyst in homogeneous solution in the presence of hydrogen peroxide alone is about 170 minutes\textsuperscript{219}. 

211
Figure 153: Plot of absorbance vs time for PCMS + NMP SCF (1:1) mole ratio FeB\(^+\): Orange (II) at pH 9.5

(Estimated error ± 5%)

Figure 154: Plot of absorbance vs time for PCMS + 0.5% DVB SCF (1:1) mole ratio FeB\(^+\): Orange (II) at pH 9.5

(Estimated error ± 5%)
Figure 155: Plot of absorbance vs time for PCMS+NMP SCF FeB\(^1\) exposure to \(\text{H}_2\text{O}_2\) over times, pH 9.5 at pH 9.5 after exposure to hydrogen peroxide for 3 hours

(Estimated error ± 5%)

Figure 156: Plot of absorbance vs time for Copolymer + 0.5% DVB SCF (1:1) mole ratio FeB\(^1\): Orange (II) at pH 9.5

(Estimated error ± 5%)
Figure 157: Plot of absorbance vs time for PCMS+NMP (0.5% DVB) SCF FeB\(^1\): Orange (II) at pH 9.5 after exposure to hydrogen peroxide for 3 hours

(Estimated error ± 5%)

Figure 158: Plot of absorbance vs time for Copolymer+0.5% DVB SCF (1:1) mole ratio FeB\(^1\): Orange (II) at pH 9.5 after exposure to hydrogen peroxide for 3 hours

(Estimated error ± 5%)
The performance for these three selected membranes containing adsorbed FeB\textsuperscript{I} was carried out at pH 11. The three SCFs used were 100 µm thick polymer on polypropylene backing with 1.0 x 10\textsuperscript{-6} µmole of catalyst adsorbed (i.e. mole ratio of catalyst: dye, 1:1). The conditions used for the bleaching experiments are listed in Table 50 and the results for the PCMS +NMP (diaminohexane cross-linked) polymer films are presented in Figure 159. Three consecutive bleaching experiments were conducted with this SCF to obtain some information about the lifetime of the catalyst under these conditions. In homogeneous solution, FeB\textsuperscript{I} catalyses oxidations at a much slower rate than at pH 9.5 (1.75 x10\textsuperscript{-7})\textsuperscript{219}. The same general trend towards longer time is also observed for the anchored catalyst, with complete bleaching taking about 540 s initially instead of 420 s at pH 9.5. However, this is not such a big difference as is observed in homogeneous solution. Clearly the catalyst behaves differently when adsorbed onto the SCF and different factors (such as transport of the dye molecules to the catalyst centres) are expected to influence the overall rate of reaction. As for the reactions at pH 9.5, the time it took for complete bleaching increased as the number of bleaching runs increased. To ensure that no FeB\textsuperscript{I} was leached into the solution during these bleaching reactions, the SCF was removed from one bleaching run for a set period of time and then replaced. As shown in Figure 160 the bleaching stopped when the SCF was removed and resumed when it was returned, showing essentially no catalyst was leached into solution during the reaction.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>20.0</td>
<td>2.0 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>1.0 x 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>FeB\textsuperscript{I}</td>
<td>On membrane</td>
<td>1.0 x 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 49: Condition of bleaching using PCMS+NMP, PCSM+0.5% DVB, Copolymer +0.5% DVB mole ratio (1:1) with FeB\textsuperscript{I}: Orange (II) at pH 11.0 with 1mM H\textsubscript{2}O\textsubscript{2}.  

215
Figure 159: Plot of absorbance vs time for PCMS + NMP SCF (1:1) mole ratio FeB\textsuperscript{1}: Orange (II) at pH 11.0

(Estimated error ± 5%)

Figure 160: Plot of absorbance vs time for PCMS + NMP SCF + FeB\textsuperscript{1} at pH 11 SCF removed at 0.5 minute and returned 2 minute later.

(Estimated error ± 5%)
The same experiments were then carried out, except that a SCF prepared using PCMS cross-linked with DVB was used to anchor the FeB\(^{1}\) catalyst. The conditions used are summarised in Table 50 and the results are presented in Figures 161 and 163).

![Graph](image)

Figure 161: Plot of absorbance vs time for PCMS +0.5% DVB SCF (1:1) mole ratio FeB\(^{1}\): Orange (II) at pH 11.0

(Estimated error ± 5%)

![Graph](image)

Figure 162: Plot of absorbance vs time for PCMS +0.5% DVB for FeB\(^{1}\) pH 11 removed from solution at 1 min and returned at 4 min.

(Estimated error ± 5%)
A very similar spread of times for the three consecutive bleaching runs were obtained (Figure 161 and 163) and again no indication of catalyst leaching from the SCF was obtained (Figure 162 and 164). Under these conditions, the two SCFs appeared to have very similar performances.

Figure 163: Plot of absorbance vs time for Copolymer +0.5% DVB SCF (1:1) mole ratio FeB⁺: Orange (II) at pH 11.0

(Estimated error ± 5%)

Figure 164: Plot of absorbance vs time for Copolymer +0.5% DVB membrane and out pH 11

(Estimated error ± 5%)
These results show that no significant leaching took place and the bleaching reaction using the SCF with FeB$^I$ occurred faster at pH 9.5 than at pH 11.

Since FeB$^I$ has been shown to be remarkably stable in acid conditions, investigations were carried out to see whether any significant bleaching would occur at pH 6. The conditions used are given in Table 50 and the results are shown in Figure 165. Very minimal (if any) bleaching occurred over a 3 hour period. Clearly for any catalytic oxidation of the dye to occur using the SCFs, the pH needs to be 7 or higher.

**Conditions:**

<table>
<thead>
<tr>
<th>FeB$^I$: Orange (II) mole ratio</th>
<th>[Phosphate buffer]</th>
<th>Orange (II)</th>
<th>FeB$^*$</th>
<th>[H$_2$O$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:1</td>
<td>0.01 M, pH 6</td>
<td>20.0 µmole</td>
<td>1.0 µmole</td>
<td>1.0 mM</td>
</tr>
</tbody>
</table>

Table 50: Condition of bleaching using PCMS+NMP SCF mole ratio (1:1) with FeB$^I$: Orange (II) at pH 6.0 with 1.0 mM H$_2$O$_2$.

Although these reactions with FeB$^I$ show that the SCF can be used with oxidation catalysts other than FeB$^*$, it was important to show that catalysts other than Fe-TAMLs could be used with the SCFs. Therefore, the use of the readily available compounds ammonium molybdate and sodium tungstate as catalysts with the SCFs was investigated. These compounds have been reported to catalyse oxidations with hydrogen peroxide, although the concentration of hydrogen peroxide.
peroxide used is usually up to 30%. Before catalytic oxidations with these catalysts on the SCFs were investigated, studies in homogenous solution were carried out with hydrogen peroxide concentrations of 1.0 mM. The first homogenous experiment was done at pH 9.5 using Orange (II) dye. The conditions used for the molybdate catalyst are shown in Table 51 and the results obtained are presented in Figure 166.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 51: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with Ammonium molybdate: Orange (II) at pH 9.5 with 1mM H₂O₂.

After 90 mins the absorbance of the dye had only dropped to 0.47, indicating that oxidation was very slow under these conditions. Since it has been reported that ammonium molybdate can catalyse the oxidation of the dye phenolphthalein with hydrogen peroxide relatively quickly, the oxidation of this dye at pH 10.5 was investigated in homogeneous solution. The conditions are given in Table 52 and the results presented in Figure 167. It can be seen that
under these conditions most of the phenolphthalein is bleached over a period of 30-40 mins. It was therefore decided to test the ability of ammonium molybdate adsorbed onto a SCF to catalyse the oxidation of phenolphthalein under similar conditions. The conditions used are summarised in Table 53 and the results presented in Figure 168.

Surprisingly, the dye was oxidised in about the same time as it was under homogeneous conditions. This indicated that transport of the dye to the catalyst was probably not the rate-limiting step, but rather the oxidation of the dye by the activated catalyst was rate-limiting. The rate for bleaching of this dye with ammonium molybdate was much slower than with the FeTAML catalysts, as expected. Nevertheless, the catalyst remained active and a duplicate bleaching run with the same SCF showed identical results to the first run. Although the catalyst was slower to oxidise the dye it is quite possible that it might remain active much longer on the SCF than do the FeTAML catalysts.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 52: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with ammonium molybdate: phenolphthalein at pH 10.5 with 1mM H₂O₂ in homogeneous system
Table 53: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with ammonium molybdate: phenolphthalein at pH 10.5 with 1mM H₂O₂ on SCF in heterogeneous system

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>On membrane</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>stirring speed</td>
<td>750 rpm</td>
<td></td>
</tr>
</tbody>
</table>

Figure 167: Plot of absorbance vs time for PCMS+NMP membrane (1:1) mole ratio ammonium molybdate: phenolphthalein at pH 10.5

(Estimated error ± 5%)
Experiments were then carried out to see if this SCF could be recycled after its use in the above experiments and after it had been exposed to hydrogen peroxide under the same condition as with catalyst (FeB*), i.e. immersed in 1.0 mM H$_2$O$_2$ for 1 hour. The results are presented in Figure 169. The catalytic activity seemed unchanged after immersion in the hydrogen peroxide solution suggesting this catalyst was robust and not degraded by this treatment.

![Figure 168: Plot of absorbance vs time for PCMS +NMP SCF (1:1) mole ratio ammonium molybdate: phenolphthalein at pH 10.5 with catalyst on the SCF](image1)

(Estimated error ± 5%)

Experiments were then carried out to see if this SCF could be recycled after its use in the above experiments and after it had been exposed to hydrogen peroxide under the same condition as with catalyst (FeB*), i.e. immersed in 1.0 mM H$_2$O$_2$ for 1 hour. The results are presented in Figure 169. The catalytic activity seemed unchanged after immersion in the hydrogen peroxide solution suggesting this catalyst was robust and not degraded by this treatment.

![Figure 169: Plot of absorbance vs time for PCMS +NMP (1:1) mole ratio ammonium molybdate: phenolphthalein at pH 10.5 after exposure to H$_2$O$_2$ for 1 hour](image2)

(Estimated error ± 5%)
The experiments described above with ammonium molybdate were then repeated with sodium tungstate. The conditions used for the bleaching experiments are collected in Tables 54–55 and the results are displayed in Figures 170–171. Figure 170 shows that at pH 10.5 the sodium tungstate in homogeneous solution does not catalyse the bleaching of orange II very quickly at all and thus has similar performance to ammonium molybdate in this respect. When the sodium tungstate was adsorbed onto the SCF it performed in a very similar manner to the ammonium molybdate with complete bleaching of phenolphthalein occurring in about 40 minutes and identical performance being observed in a duplicate experiment with the same SCF.

Confirmation that no tungstate leached from the SCF during the oxidation reactions was provided by monitoring the absorbance of the solution during a bleaching experiment in which the SCF was removed from the solution for a set time and then returned. The results are given in Figure 172. It can be seen that no observable bleaching occurred while the SCF was absent from the solution, indicating no leaching from the SCF occurred.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
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<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Sodium tungstate</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 54: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with sodium tungstate: Orange II at pH 10.5 with 1mM H₂O₂ in homogeneous system

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
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<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>2.0 × 10⁻³</td>
</tr>
<tr>
<td>Sodium tungstate</td>
<td>20.0</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>On membrane</td>
<td>1.0 × 10⁻⁶</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 55: Condition of bleaching using PCMS+NMP, mole ratio (1:1) with sodium tungstate: phenolphthalein at pH 10.5 with 1mM H₂O₂ on SCF
Figure 170: Plot of absorbance vs time for PCMS +NMP membrane (1:1) mole ratio sodium tungstate dihydrate: Orange (II) at pH 10.5
(Estimated error ± 5%)

Figure 171: Plot of absorbance vs time for PCMS +NMP membrane (1:1) mole ratio sodium tungstate: phenolphthalein at pH 10.5
(Estimated error ± 5%)
Bleaching experiments of phenolphthalein were also investigated using FeB* adsorbed onto SCFs. Three consecutive bleaching experiments were carried out using the conditions in Table 56. This was done so a comparison could be made with the corresponding ammonium molybdate or sodium tungstate catalysed reactions. The result are plotted in Figure 173 and Figure 172.

Figure 172: Plot of absorbance vs time for PCMS +NMP membrane (1:1) mole ratio sodium tungstate: phenolphthalein at pH 10.5, SCF removed from solution at 6 minute and returned back at 18 minute.

(Estimated error ± 5%)

Figure 173: Plot of absorbance vs time for PCMS +NMP, (10:1) FeB*: phenolphthalein mole ratio pH 10.5 with 1.0 mM \( \text{H}_2\text{O}_2 \)

(Estimated error ± 5%)

Bleaching experiments of phenolphthalein were also investigated using FeB* adsorbed onto SCFs. Three consecutive bleaching experiments were carried out using the conditions in Table 56. This was done so a comparison could be made with the corresponding ammonium molybdate or sodium tungstate catalysed reactions. The result are plotted in Figure 173 and Figure 172.
show that the FeB* catalysed oxidations of phenolphthalein proceed very much faster (ca. 2 minutes) than those catalysed by molybdate of tungstate (ca. 40 minutes).

3.2.3 Conclusions regarding the oxidations carried out using the beaker system

The results of the dye bleaching experiments carried out with the SCFs immersed in a solution of dye and hydrogen peroxide buffered at neutral or alkaline pH demonstrate that oxidation catalysts anchored on the films can still operate effectively and catalyse dye bleaching reactions.

Studies were carried out of the influence a range of parameters had on the catalytic performance of the SCFs. The effect on catalytic performance of changes made to the amount of catalyst adsorbed onto the SCFs, the speed of stirring, the pH of the solution, the nature of the dye, the nature of the polymer used to form the SCFs, the nature of the catalyst, and the concentration of the hydrogen peroxide were all investigated.

This smart catalytic film can catalyse bleaching reactions of dyes at pH 7 (phosphate buffer, 250 µm) with catalyst loading range from (1:1) mole ratio to (80:1) mole ratio of catalyst to dyes. Initial rate (mol L⁻¹ s⁻¹) increased (from $1.95652 \times 10^{-7}$ to $1.58696 \times 10^{-6}$) linearly until the catalyst loading reached (40:1) mole ratio. Beyond that, increasing the mole ratio no longer increase the initial rate which suggested the rate determining step is rather the transport of Orange (II) dye to the SCF surface.

For SCFs constructed from PCMS cross-linked with 1,6-diaminohexane (nominal thickness 250 µm), immersed in carbonate buffer (0.010 M, 20 mL) at pH 9.5 containing hydrogen peroxide (1.0 mM) and orange II (50 µM, 1.0 µmole), stirred at 750 rpm, the effect of changing catalyst loading was studied. The amount of FeB* catalyst adsorbed onto the SCF was changed

<table>
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<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>moles</th>
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<tbody>
<tr>
<td>H₂O₂</td>
<td>20.0</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>FeB*</td>
<td>20.0</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>20.0</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 56: Condition of bleaching using PCMS+NMP, mole ratio (10:1) with FeB*: phenolphthalein at pH 10.5 with 1mM H₂O₂ on SCF
in steps from 1 μmoles (i.e. catalyst: dye mole ratio, 1:1) through to 140 μmole (i.e. catalyst: dye mole ratio, 140:1). The initial rate of dye oxidation increased linearly from $9.52 \times 10^{-8}$ to $1.20 \times 10^{-5}$ mol L$^{-1}$ s$^{-1}$ with the amount of adsorbed catalyst until the catalyst loading reached approximately 140 μmole (i.e. catalyst: dye mole ratio, 100:1). Beyond this point increasing the amount of catalyst had no effect on the rate of bleaching (see Figure 123). This suggests that after this point the rate-limiting step was no longer determined by the rate at which the anchored catalyst could oxidise the dye, but instead was determined by the transport of the dye to the active catalyst site. As would be expected for an immobilised catalyst, the rate of bleaching of orange II catalysed by FeB$^*$ (for 1:1 mole ratio of catalyst: dye, rate was $9.52 \times 10^{-8}$ mol L$^{-1}$ s$^{-1}$) was considerably slower than the rate for equivalent amounts of catalyst present in homogeneous solution ($2 \times 10^{-7}$ mol L$^{-1}$ s$^{-1}$)$^{219}$

The effect of stirring rate on the rate of orange II dye oxidation was also investigated. For a set bleaching reactions using the same conditions as above but with the amount of adsorbed FeB$^*$ held constant at 1.0 μmoles (i.e. catalyst:dye mole ratio, 1:1), it was found that as the stirring rate increased from 100 to 750 rpm the time for complete bleaching decreased (see Figures 136). However, increasing the stirring speed further to 1000 rpm did not have any further effect. These results indicate the bulk transport of the dye to the SCF surface can be a rate-limiting step at slower stirring speeds. At speeds above 750 rpm other processes become rate-limiting. This result also indicate that the same pattern but the reaction completed at faster initial rate as expected since the catalyst can normally operate between pH (9.5 &11)$^{219}$.

Oxidation experiments with the SCFs were also carried out at different pH values. The results obtained using similar conditions to those above but with the solutions buffered at pH 6.0, 7.0, 9.5 and 11.0 showed that for FeB$^*$ the time for complete oxidation of the dye increased as the pH became more alkaline (see Figures 122, 124, 131 and 135). Catalytic bleaching was not observed at the acidic pH of 6.0. This is the same trend that is observed for oxidations catalysed by FeB$^*$ in homogeneous solution where the maximum rate of oxidation is observed at close to pH 11 and the rate is extremely slow at pH 6.

The effect of changes to the concentration of hydrogen peroxide was also investigated. It was found that on changing the concentration of hydrogen peroxide from 1.0 mM to 0.01 mM catalytic bleaching of orange II still occurred at a very similar rate (see Figures 131,146 and 148) indicating that hydrogen peroxide delivery to the catalyst is not a rate limiting-step in these reactions. Reduction of the concentration further to 0.001 mM was also studied. At this
level, the number of moles of hydrogen peroxide present was only 0.2 the number of moles of dye. Surprisingly the absorbance of the dye slowly dropped from 1.0 to 0.8 over about 10 minutes, suggesting that under these conditions the rate of reaction was much slower, but that the utilisation of hydrogen peroxide was quite efficient.

The oxidation reactions of different dyes were also explored to determine if the nature of the dye or the electrostatic charge of the dye in alkaline solution were important factors in determining rates of dye oxidation. In addition to experiments with orange II, bleaching reactions of pinacyanol chloride, phenolphthalein and safranine O were investigated. Of these four dyes, pinacyanol chloride and safranine O are cationic, while the other two are negatively charged in alkaline solution. Since the SCFs contained quaternary ammonium cationic groups as part of the functionalised polymer, it was important to ascertain that both positively and negatively charged species could reach the catalytic sites within the SCF and undergo oxidation. The dyes orange II, pinacyanol chloride and safranine O were indeed catalytically oxidised by the SCF containing FeB* as the catalyst. The rates of oxidation of the dyes followed the same trend in the rates that was observed in homogeneous solution, i.e. safranine O < orange II < pinacyanol chloride. It therefore appeared that the electrostatic charge of the dye did not unduly influence the rate of oxidation catalysed by the FeB* in the SCFs.

To confirm that the SCFs would operate successfully with oxidation catalysts other than FeB*, SCFs with adsorbed FeBJ, ammonium molybdate, or sodium tungstate were also investigated. Catalytic bleaching was observed for SCFs containing FeBJ, and the rates of oxidation of dyes at pH 9.5 were similar to, or slightly faster than, the rates observed for oxidations with FeB*adsorbed on SCFs. This is very similar to the situation in homogeneous solution where it has been shown that orange II is catalytically oxidised at a slightly faster rate (ca. 1.3 times faster) by FeBJ.219. FeB* and FeBJ are both iron-TAMLs, and so it was important to demonstrate that SCFs containing very different oxidation catalysts would also be effective. Therefore, films with adsorbed ammonium molybdate or sodium tungstate were synthesised and investigated.

It was found that the dye phenolphthalein was catalytically oxidised by these SCFs at a slow rate. This demonstrated that other oxidation catalysts can be used with the SCFs, although the iron-TAMLs give greatly superior rates of oxidation.

Although it was shown that the oxidation catalysts do not leach from the SCF after they have been adsorbed and washed well with buffer solution, it was also essential to demonstrate that no catalyst was displaced from the SCFs during the oxidation reactions, since this would result in homogeneous catalysis which is known to occur at a very fast rate. To do this, experiments
were carried out in which part way through a bleaching reaction the SCF was removed from
the solution for a set time and then returned to the solution. Continuous monitoring of the
absorbance of the solution showed that when the SCF was removed from the solution
essentially no bleaching of the dye occurred (absorbance remained nearly constant), but when
it was returned bleaching resumed. These simple experiments proved that negligible amounts
of any of the catalysts studied were displaced from the SCF during bleaching experiments.

Information was also obtained about the long-term stability of the catalyst on the SCFs during
extended periods of catalytic bleaching. To carry out these studies, 10 consecutive bleaching
experiments were carried out on the same SCF and the absorbance vs time plots for each of the
10 bleaching experiment compared. Remarkably the results showed that in some cases no loss
of activity was observed in the catalyst on the SCF over 10 consecutive runs (see Figure 124).
In most other cases the catalyst appeared to slowly degrade to some extent over the 10
experiments. The SCF constructed with PCMS polymers cross-linked with 1,6-diaminohexane
gave the best results in general. Significant activity was still retained in all cases after the 10th
reaction. In these experiments the total time the catalyst was in contact with hydrogen peroxide
was 200 – 300 minutes. For significant activity to still remain after this time is quite
remarkable. In comparison, in homogeneous solution FeB* at pH 9.4 has a half-life of only
about 10-15 minutes when exposed to similar levels of hydrogen peroxide 219 Clearly the
immobilised catalyst is much more stable and a contributing factor will be that intermolecular
oxidative degradation of the catalyst will be suppressed when it is immobilised.

To further study the stability of the catalyst on the SCF in the presence of hydrogen peroxide
but in the absence of substrate to oxidise, the SCFs were immersed in hydrogen peroxide for
set periods and then the catalytic activity of the films measured by determining the rate at which
they could catalyse the oxidation of orange II. For example, a PCMS film cross-linked with
1,6-diaminohexane and containing 1 µmole of FeB* (i.e. catalyst: dye mole ration 1:1 for each
bleaching experiment) was immersed in 1.0 mM hydrogen peroxide for 1.5 hours, removed,
rinsed and then used in a standard catalytic bleaching experiment with orange II. At the
conclusion of this experiment it was then taken out of the solution, rinsed and then the
immersion in hydrogen peroxide followed by a bleaching process repeated four times.
Although this treatment slowly reduced the catalytic activity of the SCF, complete bleaching
of the orange II solution was still observed after the four cycles (e.g. see Figure 127). This
further demonstrates the stability of the FeB* catalyst when adsorbed onto the SCFs.
One final experiment was carried out to obtain information about the stability of the oxidised catalyst when it is adsorbed onto the SCF. A SCF containing 80 μmoles of FeB* was immersed in 0.1 mM hydrogen peroxide solution at pH 9.5 for 1 hour, removed, rinsed and then used for a typical orange II bleaching experiment. The pre-oxidised catalyst in the SCF completely bleached the orange II dye in ca. 2.5-4 minutes showing that the catalyst can be activated to a highly oxidising form and remain unchanged in that form for tens of minutes without undergoing degradation.
3.3 Catalytic oxidation experiments with a “U-tube” apparatus

As described above, it was established with the experiments involving the SCFs in beakers that the homogeneous oxidation catalysts still operated when immobilised on a SCF, that the catalysts were not leached from the SCF during catalytic oxidation reactions and that the catalyst molecules were long-lived on the SCF. Therefore attention was then turned to investigating the performance of the SCFs in situations where the hydrogen peroxide and base is separated from the solution containing the substrate to be oxidised. It is in this type of arrangement that the SCFs were designed to operate. A simple system that was devised to carry out these tests was a glass “U-tube” with a joint in the middle section with seals between which a SCF could be clamped.

This section focuses on experiments using two SCF membranes of different nominal thickness, 100 µm and 250 µm, where the 100 µm thick membrane was initially used to prove the principle that the SCFs developed were able to operate in this more complex system. The thicker SCFs were then studied in more depth because they could anchor more catalyst and did not contain defects such as pin holes through which bulk solution could flow. Similar to the studies using beakers, a series of blank experiments were first carried out to evaluate that the bleaching observed was only caused by the SCF system and not because of other factors such as simple absorption. Three U-tubes of different diameters (2, 3 and 7 cm) were used but most experiments were conducted with a system with 3 cm diameter tubes. A schematic drawing of the U-tube apparatus is given in Figure 174.

Schematic diagram of U-tubes
The first blank reaction performed was to ensure that the concentration of the H$_2$O$_2$ did not decrease appreciably over time and to show that only very small amounts of H$_2$O$_2$ passed through the membrane from the permeate side to the retentate side.

This was done by placing 400 mL of carbonate buffer at pH 9.5 containing H$_2$O$_2$ (1.0 mM) on one side and 100 mL of carbonate buffer at pH 9.5 on the other side. A SF (PCMS +NMP) was used. The hydrogen peroxide concentration of the permeate solution (initially 400 mL) was monitored using H$_2$O$_2$ test strips. After 5 hours, the H$_2$O$_2$ concentration remained at 35 ppm while the solution was stirred using stir bars rotating at 1000 rpm on both sides. The experiment was left to continue overnight. Over this 24 hour period 150 mL of the hydrogen peroxide solution passed through the membrane using H$_2$O$_2$ test strips. After 5 hours, H$_2$O$_2$ concentration remained at 35 ppm while the solution was stirred using stir bars rotating at 1000 rpm on both sides. The experiment was left to continue overnight. Over this 24 hour period 150 mL of the hydrogen peroxide solution passed through the membrane and the heights of the two solutions had equilibrated.

Figure 175: schematic diagram of medium u-tube prototype
Since the hydrogen peroxide is only required to activate the catalyst in very small amounts, experiments were carried out with SCFs containing FeB* catalyst, hydrogen peroxide solution placed on one side of the SCF and dye solution on the other. The aim was to see if any significant bleaching occurred when the levels of the two solutions were the same and hence there was no hydrostatic head to drive the hydrogen peroxide very slowly through the film. The conditions are summarised in Table 5.7.

The absorbance was monitored for ca. 2 hours before being left to run overnight. The results are presented in Figure 1.78.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>Moles</th>
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<tbody>
<tr>
<td>H₂O₂</td>
<td>100.0</td>
<td>1.0 × 10⁻⁴</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>30.0</td>
<td>1.5 × 10⁻⁶</td>
</tr>
<tr>
<td>(FeB*) on smart film</td>
<td></td>
<td>1.5 × 10⁻⁶</td>
</tr>
<tr>
<td>Stirring speed</td>
<td></td>
<td>500-750 rpm</td>
</tr>
</tbody>
</table>

Table 5.7: bleaching condition in u-tube (1:1) mole ratio pH 9.5, 1.0 mM H₂O₂
This was an encouraging result as the absorbance of the dye dropped significantly over the 2 hours, suggesting some catalytic bleaching was occurring, even though the hydrogen peroxide had no pressure incentive to flow through the SCF. During this 3 hours, the absorbance of the hydrogen peroxide solution remained zero showing that no unbleached dye diffused through the SCF.

A blank experiment was also carried out using the U-tube apparatus with a SCF that contained no Fe-TAML catalyst. Hydrogen peroxide was placed in one arm and dye solution in the other. The height of the peroxide solution was 14.0 cm above the dye solution. The conditions are

Figure 177: Plot of absorbance vs time for PCMS+NMP membrane without FeB* pH 9.5

Figure 178: Plot of absorbance vs time for (1:1) mole ratio pH 9.
summarised in Table 59. Over 3 hours the absorbance of the dye solution only dropped from 0.9 to 0.85 (see Figure 178). This shows that in the absence of the catalyst minimal amounts of dye are oxidised (or adsorbed onto the SCF) over 3 hours.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>100.0</td>
<td>1.0 × 10⁻⁴</td>
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<tr>
<td>Orange (II)</td>
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</tr>
<tr>
<td>Stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 58: blank condition in u-tube pH 9.5, 1.0 mM H₂O₂

Another blank reaction was performed to ensure that no decrease in the absorbance occurred in a similar experiment in which FeB* was present on the SCF and no hydrogen peroxide was present at all in the solution. Very similar results were obtained (see Figure 179) and the same very small initial drop in absorbance was almost certainly due to the adsorption of a small portion of the dye on the membrane which visibly turned slightly orange. Condition was summarized in Table 59.

<table>
<thead>
<tr>
<th>Chemicals</th>
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<th>Moles</th>
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<tbody>
<tr>
<td>Orange (II)</td>
<td>30.0</td>
<td>1.5 × 10⁻⁶</td>
</tr>
<tr>
<td>(FeB*)</td>
<td>On smart film</td>
<td>1.5 × 10⁻⁶</td>
</tr>
<tr>
<td>Stirring speed</td>
<td></td>
<td>750 rpm</td>
</tr>
</tbody>
</table>

Table 59: blank condition in u-tube (1:1) mole ratio pH 9.5, 1.0 mM H₂O₂

![Absorbance vs time for membrane PCMS+NMP with FeTAML(FeB*) catalyst and no H₂O₂](image)

Figure 179: Plot of absorbance vs time for PCMS+NMP membrane with FeB* without hydrogen peroxide
Once the blank experiments had been carried out, actual reactions were carried out using a (1:1) mole ratio of (FeB*) and Orange (II) in the presence of hydrogen peroxide in one arm and the dye in the other.

All the reaction conditions are summarised in Table 60 and the results are given in Figure 180.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume (mL)</th>
<th>Moles</th>
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<tbody>
<tr>
<td>H₂O₂</td>
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</tr>
<tr>
<td>Orange (II)</td>
<td>30.0</td>
<td>1.5 × 10⁻⁶</td>
</tr>
<tr>
<td>(FeB*)</td>
<td>On smart film</td>
<td>1.5 × 10⁻⁶</td>
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<tr>
<td>Stirring speed</td>
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<tr>
<td></td>
<td>Final=11.0 cm</td>
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</table>

Table 60: bleaching condition in u-tube (1:1) mole ratio pH 9.5 using stirring rate 1000 on Orange (II) side and 700 rpm on hydrogen peroxide side.

Nearly all the orange II dye was bleached over a period of two hours. It was discovered that after 3 hours, only about 4 mL of the hydrogen peroxide solution had passed through the membrane into the other side. These results showed that in principle the SCFs could indeed be used in the way they were originally intended, i.e. to oxidise substrates in a solution without gross contamination of the substrate solution with catalyst, base or hydrogen peroxide. When
the system was left to stand overnight the total water volume of hydrogen peroxide and carbonate buffer that passed through the SCF was 29 mL. Also, although the initial H\(_2\)O\(_2\) concentration was 30 mg/L the H\(_2\)O\(_2\) concentration had dropped to 10 mg/L after this time. However, no H\(_2\)O\(_2\) was detected on the dye side. The catalyst loading was then varied to investigate if more catalyst would increase the rate of the reaction. Experiments were then conducted with both solutions buffered at pH ca. 7 to see whether the SCFs could still carry out bleaching at this environmentally significant pH. Comparisons could also then be made the SCFs in the beaker experiments and with the homogenous system. The conditions used and results obtained are shown in Table 61-62 and Figure 181, respectively.

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<tr>
<th>Chemicals</th>
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</tr>
<tr>
<td>Orange (II)</td>
<td>30.0</td>
<td>1.5 × 10(^{-6})</td>
</tr>
<tr>
<td>FeB*</td>
<td>On smart film</td>
<td>30.0 × 10(^{-6})</td>
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<table>
<thead>
<tr>
<th>Stirring speed</th>
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<tr>
<td>Height difference</td>
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<tr>
<td></td>
<td>Final = 14.0 cm</td>
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</table>

Table 61: Bleaching condition in u-tube (20:1) mole ratio pH 7.1 using stirring rate 1000 on Orange (II) side and 700 rpm on hydrogen peroxide side.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Volume (mL)</th>
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<tr>
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<td>1.0 × 10(^{-4})</td>
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<tr>
<td>Orange (II)</td>
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<td>FeB*</td>
<td>On smart film</td>
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<td></td>
<td>Final = 11.0 cm</td>
</tr>
</tbody>
</table>

Table 62: Bleaching condition in u-tube (80:1) mole ratio pH 7.1 using stirring rate 1000 on Orange (II) side and 700 rpm on hydrogen peroxide side.
This result shows that by increasing the loading of the FeB* catalyst from 20 µmole to 80 µmole, increased the initial rate of the reaction at pH 7, but it is still quite slow compared to the reactions at pH 9.5 ($1.2 \times 10^{-5}$ mol L$^{-1}$ s$^{-1}$, respectively). Unfortunately, only 2 data points were obtained because of time constraints.

Since it was discovered that the stirring speed had a significant impact on the bleaching time for the experiments in a beaker, experiments were conducted using a PCMS+NMP SCF (nominally 100 µm thick) with $120 \times 10^{-6}$ moles of FeB* on the SCF (a catalyst to dye ratio of 120 µmole:1.5µmole) with both solutions buffered at pH 9.5.

The stirring speeds of both the dye and the hydrogen peroxide solutions were varied together from 100 rpm -1000 rpm. Although both solutions were stirred it would be expected that only the dye solution actually needed stirring. The results are presented in Figures 182 and 183. Clearly increasing the stirring rate increased the rate at which bleaching occurred up to about 750 rpm. As with the beaker experiments bulk transport of the dye to the SCF can play an important role in determining the overall rate of the bleaching reaction.

Under these conditions the bleaching experiment was completed in 100 minutes at pH 9.5 when the stirring speed was 1000 rpm.
Figure 182: Plot of absorbance vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H$_2$O$_2$ for different stirring speed.

Figure 183: Plot of absorbance vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H$_2$O$_2$ for different stirring speed. Plot of different stirring speed vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H$_2$O$_2$. 

Figure 183: Plot of absorbance vs time for (80:1) mole ratio at pH 9.5, 1.0 mM H$_2$O$_2$ for different stirring speed.
Next, the same bleaching experiment using identical conditions was repeated except the pH of both solutions was buffered at 11. The results are presented in Figure 184-185.

Figure 184: Plot of absorbance vs time for (80:1) mole ratio at pH 11.0, 1.0 mM H₂O₂ for different stirring speed

Figure 185: Plot of different stirring speed vs time for complete bleaching at pH 11.0, 1.0 mM H₂O₂

At pH 11, the time for complete bleaching also increased with increasing stirring rate and this time the minimum time for bleaching occurred for the fastest stirring speed of 1000 rpm. At this speed complete bleaching occurred in 30 minutes, which is considerably faster than the bleaching reactions at lower pH values. Given the successful operation of the SCFs in the U-tube apparatus with the both the dye and hydrogen peroxide solutions buffered at pH 11, the
experimental conditions were altered so that the pH of the dye was 7 while the pH of the hydrogen peroxide was buffered to either pH 9.5 or 11 while all the other conditions remained the same as in the experiments above. This was a key experiment, because it completely replicates the general conditions that the SCFs would operate under if they were employed in real-world situations to treat large volumes of water, that were at a pH of close to 7. The conditions are given in Table 63 and the results are presented in Figure 186. The results obtained when both solutions were at pH 7 or 9.5 are included in this Figure for comparative purposes. All experiments utilised a SCF (PCMS+NMP with 120 µmole of anchored FeB*) nominally 250 µm thick. The conditions are given in Table 63 and the results are presented in Figure 186.
Diameter of SCF = 35 mm, [Carbonate buffer] = 0.01 M, stirring speed = 1000 rpm both sides  I = initial, F = final

FeB* anchored on membrane = \((1.2 \times 10^{-4})\) moles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume (mL)</th>
<th>Moles</th>
<th>pH</th>
<th>pH</th>
<th>pH</th>
<th>pH</th>
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<tbody>
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<td></td>
<td></td>
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<td>Experiment 1</td>
<td>Experiment 2</td>
<td>Experiment 3</td>
<td>Experiment 4</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>100.0</td>
<td>(1.0 \times 10^{-4})</td>
<td>(I) = 11.0</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>(I) = 9.5</td>
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<tr>
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<td>(F) = 7.0</td>
<td>(F) = 9.5</td>
<td>(F) = 9.5</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>30.0</td>
<td>(1.5 \times 10^{-6})</td>
<td>(I) = 7.0</td>
<td>(I) = 7.0</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(F) = 8.0</td>
<td>(F) = 7.0</td>
<td>(F) = 8.0</td>
<td>(F) = 9.5</td>
</tr>
</tbody>
</table>

| Height difference | Initial = 13.25 cm | Final = 11.20 cm |

Table 63: bleaching condition in u-tube (80:1) mole ratio at various pH using stirring rate 1000 on both sides
Importantly, the dye was still bleached fairly quickly when the pH of the dye solution was 7 and the hydrogen peroxide solution was buffered at either pH 9.5 or 11. With the dye solution at pH 7 and peroxide at pH 11 complete bleaching occurred in about 60 minutes. This compares with a time of 30 minutes when the pH of both solutions was 11 (Figure 186) or >100 minutes when the pH of both solutions was 9.5.

Since experiments in the beakers indicated that using SCFs with nominal thickness of 250 μm was advantageous, the experiments above were repeated using SCFs of this thickness with an increased number of moles of FeB* adsorbed (2.1 x 10^-4 moles, catalyst: dye mole ration 140:1). The experimental conditions and results are shown below in Table 64 and Figure 187, respectively. The times taken for complete bleaching with the dye and hydrogen peroxide solutions at different pH values are collected in Table 65.
Diameter of SCF = 35 mm, [Carbonate buffer] = 0.01 M, stirring speed = 1000 rpm both sides I = initial, F = final

FeB* anchored on membrane = \((2.1 \times 10^{-4})\) moles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume (mL)</th>
<th>Moles</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experiment 1</td>
<td>Experiment 2</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>100.0</td>
<td>1.0 × 10⁻⁴</td>
<td>(I) = 11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F) = 11.0</td>
<td>(F) = 7.0</td>
</tr>
<tr>
<td>Orange (II)</td>
<td>30.0</td>
<td>1.5 × 10⁻⁶</td>
<td>(I) = 7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F) = 8.0</td>
<td>(F) = 7.0</td>
</tr>
</tbody>
</table>

Table 64: Bleaching condition in u-tube (140:1) mole ratio at various pH using stirring rate 1000 on both sides for 250 µm thickness

<table>
<thead>
<tr>
<th>Experiment no</th>
<th>Orange (II) side pH , (retentate)</th>
<th>H₂O₂ side pH , (permeate)</th>
<th>Complete bleaching time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.5</td>
<td>9.50</td>
<td>55.0</td>
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<tr>
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<td>11.0</td>
<td>11.0</td>
<td>30.0</td>
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<td>3</td>
<td>7.0</td>
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<tr>
<td>4</td>
<td>7.0</td>
<td>9.50</td>
<td>70.0</td>
</tr>
</tbody>
</table>

Table 65: The times taken for complete bleaching with the dye and hydrogen peroxide solutions at different pH values
Under these conditions it only took 40 minutes to completely bleach a solution of the dye at pH 7 using a hydrogen peroxide solution with pH of 11. This is considerably faster than the 60 minutes it took using 80:1 mole ratio which corresponds to $1.2 \times 10^{-4}$ moles of adsorbed FeB* showing that increasing the amount of catalyst decreased the time for complete bleaching.

Figure 187: Plot of absorbance vs time for (140:1) mole ratio at different pH combination, 1.0 mM H$_2$O$_2$ using 1000 rpm stirring speed
3.3.1 Example of photos during experiments for (80:1) mole ratio of FeB*: Orange (II) pH 9.5, hydrogen peroxide solution pH 9.5

Figure 188: Image 1 show the initial colour of orange (II) dye at time zero, image 2 show the colour of Orange (II) after 30 minute, image 3 was taken after 60 minute and image 4 was taken after 90 minute
Experiments were also conducted with the positively charged dye safranine O to determine whether bleaching of this dye would still occur when the SCF was used in the U-tube apparatus. Exactly the same conditions as those above were used and these are summarised in Table 66-67. The results obtained are given in Figure 189.

The first important observation is that the SCF in the U-tube configuration could also catalyse the bleaching of this dye. As noted before, the rate of catalytic bleaching of this dye is slower than that of orange II when the reactions are carried out in homogenous solution. It is therefore somewhat surprising that time for complete bleaching was essentially the same (60 minutes) whether the pH of the dye and hydrogen peroxide solutions were 9.5 and 9.5, 11.0 and 11.0 or 7.0 and 11.0, respectively in each case (see Table 67). In the final entry in Table 67 for pHs of 7.0 and 9.5, the time was much longer at 150 minutes. This result followed the expected trend, i.e. that when the base was decreased sufficiently the rate of bleaching did drop. However, the observation that the rate was the same for the other three situations strongly indicates that in these cases the rate limiting step of the reaction was not the rate of dye oxidation by the activated FeB*, but some other step such as delivery of the dye to the catalytic sites, either from the bulk solution or from within the “polymer brush” zone.

The time of 60 minutes for complete bleaching compares very favourably with the time of about 40 minutes for complete bleaching of orange II under identical conditions. In homogeneous oxidation reactions of these dyes orange II is usually bleached about 10 times faster than safranine O. Again this points to other (perhaps common) processes contributing to the rate-limiting step(s) in the catalytic oxidations with the SCFs.
Diameter of SCF = 35 mm, [Carbonate buffer] = 0.01 M, stirring speed = 1000 rpm both sides I = initial, F = final

FeB* anchored on membrane = \((2.1 \times 10^{-4})\) moles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume (mL)</th>
<th>Moles</th>
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<th></th>
<th></th>
<th></th>
</tr>
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<td>Experiment 1</td>
<td>Experiment 2</td>
<td>Experiment 3</td>
<td>Experiment 4</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>100.0</td>
<td>1.0 \times 10^{-4}</td>
<td>(I) = 11.0</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>(I) = 9.5</td>
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<td>(F) = 9.5</td>
<td>(F) = 9.5</td>
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<td>Safranine O</td>
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<td>1.5 \times 10^{-6}</td>
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<td>(I) = 7.0</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
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<td>(F) = 8.0</td>
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<td>(F) = 8.0</td>
<td>(F) = 9.5</td>
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<td></td>
<td></td>
<td>Final = 11.20 cm</td>
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</table>

Table 66: Bleaching condition in u-tube (140:1) mole ratio of FeB*: safranine O at various pH using stirring rate 1000 on both sides for 250 \(\mu\)m thickness

<table>
<thead>
<tr>
<th>Entry</th>
<th>Safranine O side pH, (retentate)</th>
<th>H₂O₂ side pH, (permeate)</th>
<th>Complete bleaching time (min)</th>
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<tr>
<td>1</td>
<td>9.5</td>
<td>9.5</td>
<td>65.0</td>
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<tr>
<td>2</td>
<td>11.0</td>
<td>11.0</td>
<td>60.0</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>11.0</td>
<td>60.0</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>9.5.0</td>
<td>150.0</td>
</tr>
</tbody>
</table>

Table 67: The times taken for complete bleaching with the dye and hydrogen peroxide solutions at different pH values
Attempts were also made to carry out catalytic oxidations in the U-tube apparatus using different catalysts. A reaction with the ammonium molybdate catalyst, \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}\), adsorbed onto a SCF was carried out and to compare these with the results obtained with FeB* and FeB^I.

The ammonium molybdate was adsorbed onto a SCF constructed from PCMS+NMP polymer with nominal thickness of 100 µm. The number of moles of ammonium molybdate adsorbed was 15 µmole (i.e. the catalyst: dye mole ratio was 10:1). The membrane was then sandwiched in U-tube glass joint and then the experiment was carried out using the conditions noted in Table 68. The pHs of the hydrogen peroxide and dye solutions were 10.5 both sides, respectively. The results are given in Figure 190.

![Absorbance vs time (min) for PCMS+NMP membrane 250 µm, (140:1) mole ratio FeB*: Safranine O in u-tube glass joint](image)

**Figure 189:** Plot of absorbance vs time for (140:1) mole ratio at different pH combination, 1.0 mM \(\text{H}_2\text{O}_2\) using 1000 rpm stirring speed

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume (mL)</th>
<th>Moles</th>
<th>[Carbonate buffer]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O}_2)</td>
<td>100.0</td>
<td>(1.0 \times 10^{-4})</td>
<td>0.01 M</td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>30.0</td>
<td>(1.5 \times 10^{-6})</td>
<td>0.01 M</td>
</tr>
<tr>
<td>((\text{NH}_4)_6\text{Mo}<em>7\text{O}</em>{24}.4\text{H}_2\text{O}))</td>
<td>On smart film</td>
<td>(1.5 \times 10^{-5})</td>
<td>0.01 M</td>
</tr>
<tr>
<td>Stirring speed</td>
<td></td>
<td></td>
<td>1000 rpm</td>
</tr>
<tr>
<td>Height difference</td>
<td>Initial = 14.7 cm</td>
<td>Final = 11.2 cm</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>pH 10.5 for both hydrogen peroxide and phenolphthalein</td>
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</tr>
</tbody>
</table>

**Table 68:** bleaching condition in u-tube (10:1) mole ratio of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O})\): phenolphthalein at pH 10.5 both sides using stirring rate 1000 rpm on both sides
The phenolphthalein was bleached essentially completely over a period of about 35 minutes which indicates that this oxidation catalyst can also be successfully used in this configuration. The time taken for complete bleaching is very similar to that observed in the beaker experiment at pH 10.5 (Figure 139), indicating that in this case performance is not reduced on switching to the U-tube configuration for bleaching with the SCF.
Experiments were also conducted with the U-tube apparatus using the catalyst FeB\textsuperscript{3} adsorbed onto the SCFs. In one set of experiments the bleaching of the positively charged pinacyanol chloride was investigated using 1.5 μmole of adsorbed catalyst (i.e. catalyst:dye mole ratio 1:1). The conditions are given in Table 69 and the results are presented in Figure191. (I) = initial and (F) = final.

Diameter of SCF = 35 mm, [Carbonate buffer] = 0.01 M, stirring speed = 1000 rpm both sides I = initial, F = final

FeB\textsuperscript{3} anchored on membrane = \( (1.5 \times 10^{-6}) \) moles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume (mL)</th>
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<th>pH</th>
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<th></th>
<th></th>
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<td></td>
<td></td>
<td>Experiment 1</td>
<td>Experiment 2</td>
<td>Experiment 3</td>
<td>Experiment 4</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>100.0</td>
<td>( 1.0 \times 10^{-4} )</td>
<td>(I) = 11.0</td>
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<td>(F) = 9.5</td>
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<tr>
<td>Pinacyanol chloride</td>
<td>30.0</td>
<td>( 1.5 \times 10^{-6} )</td>
<td>(I) = 7.0</td>
<td>(I) = 7.0</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
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<td>Initial = 13.25 cm</td>
<td>Final = 11.20 cm</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 69: Bleaching condition in u-tube (1:1) mole ratio of FeB\textsuperscript{3}: pinacyanol chloride at various pH using stirring rate 1000 on both sides for 250 μm thickness
Bleaching occurred and the time for complete reaction was about 50 minutes when the pH of the hydrogen peroxide solution was 11.0 and the pH of the dye solution was 7.0. This is almost identical to the time taken for the complete bleaching of pinacyanol chloride under the same conditions. This provides further evidence that the rate-limiting step is not oxidation of the dye by the activated catalyst.

3.3.4 Conclusion for experiments conducted in the U-tube apparatus

A series of blank reactions were carried out prior to performing the actual bleaching experiments in the U-tube apparatus. Blank reactions were carried out with all parts of the complete system except that in one case the catalyst was not included and in the other case the hydrogen peroxide was not included. In both cases essentially no bleaching occurred. There was a very small drop in absorbance of the orange II dye solution in both cases during the first 60 minutes, but no further drop over the next 3 hours. This was almost certainly due to a small amount of the dye adsorbing onto the SCF which was observed to take on a pale orange colour.

Preliminary bleaching experiments using the U-tube apparatus with all the components present showed that the dye solution that was separated from the hydrogen peroxide solution by the SCF was indeed bleached in reasonable times.

As might be expected, the rate of bleaching increased as the amount of catalyst on the SCF increased. For example with both the dye and hydrogen peroxide solutions at pH 7.0, the rate of bleaching of orange (II) increased from $1.29043 \times 10^{-6}$ to $2.16087 \times 10^{-6}$ mol L$^{-1}$ s$^{-1}$ as the amount of adsorbed
catalyst increased from 30.0 µmoles (i.e. catalyst: dye mole ratio of 20:1) to 120.0 µmoles (i.e. catalyst: dye mole ratio of 80:1) (see Figure 181).

Since the experiments with the SCFs in beakers showed the stirring speed can influence the rates of the bleaching reactions, a series of tests were also carried out with different stirring speeds in the U-tube apparatus. It was found that on increasing the stirring speed of the dye solution from 100 through to 1000 rpm, the time for complete bleaching of orange II solutions decreased from 210 to 105 minutes at pH 9.5, and from 80 to 30 minutes at pH 11.0 (see Figure 182 and 184 respectively).

Importantly it was demonstrated that the SCFs still catalysed the bleaching of dye solutions at reasonably fast rates in the U-tube apparatus when the pH of the dye solution was 7.0 and the pH of the hydrogen peroxide was either 9.5 or 11.0. These important observations indicate that the SCFs can in principle operate in the way that was intended and oxidise dilute pollutants in water without contaminating the water with excess catalyst, base or hydrogen peroxide. Complete bleaching of the dye solution occurred in about 40-60 minutes for pH 7.0 on the dye side and pH 11.0 on the hydrogen peroxide depending on the conditions used (see Figures 181 and 191).

During these catalytic bleaching experiments with the hydrogen peroxide and base separated by the SCF, the hydrogen peroxide solution is held at a higher level than the dye solution to provide a small hydrostatic head that helps to drive a small amount of hydrogen peroxide solution into the polymer membrane so the anchored catalyst molecules can be activated and subsequently oxidise the dye molecules that diffuse into the polymer brush layer. Since the formation of the functionalised polymer membranes was not optimised, even the best membranes produced were more porous than would probably be ideal. As a result, over the approximately one hour it took for complete dye oxidation about 6 mL of hydrogen peroxide solution passed through the SCF. If the unbuffered dye solution was initially at pH 7.0, this caused the pH of the dye solution to rise to about pH 7.9 after one hour. Nevertheless, the concentration of hydrogen peroxide in the dye solution was found to be less 1 ppm after one hour. Since the rate of oxidation of the dyes orange II and safranine O by the SCFs at pH 8 and hydrogen peroxide levels less than 1 ppm is negligible, it can be assumed that any hydrogen peroxide solution that passes through the SCF and into the dye solution results in minimal dye oxidation. The great majority of dye oxidation therefore must occur within the SCF as intended.

It was also shown that dyes other than the negatively charged orange II could be bleached using the SCFs in the U-tube apparatus. Solutions of the positively charged dyes safranine O and pinacyanol chloride were also effectively bleached in this system. Interestingly, the times taken to completely bleach solutions of these dyes were fairly similar (see Figures 189 and 191). This is very different to
the situation when the catalyst is in homogeneous solution where the rate of bleaching follows the order pinacyanol chloride < orange II < safranine O. This indicates that the rate-limiting step in the U-tube oxidation reactions is not the rate of oxidation of the dye by the activated catalyst, but rather another process such as transport of the dye to the catalyst sites. The dependence of the rate on stirring speed up to a limiting speed indicates that bulk transport of the dye to the SCF surface can be rate-limiting at slow stirring speeds. At fast stirring speeds it is possible that diffusion of the dye molecules to the catalyst sites within the polymer brushes could be a rate-limiting process.

As with the reactions of the SCFs that were carried out in the beakers, it was demonstrated that SCFs with different adsorbed catalysts could also operate in the U-tube apparatus. For example, films containing either adsorbed ammonium molybdate or FeB were also effective at catalysing the bleaching of dyes (see Figures 190). This demonstrates the operation of the SCFs in this configuration is not limited to one particular catalyst and that they might be used with a range of different oxidation catalysts.

3.4 Oxidation Experiments with the SCFs using a Cross-flow system

The experiments with the SCFs in the U-tube apparatus proved that surrogate pollutants (dyes) could be oxidised in water solutions without contaminating the water with large amounts of catalyst peroxide or base. In order to show that the SCFs could operate in a configuration that would more closely resemble a system that might be used in a commercial application, a “cross-flow” oxidation system was designed and tested. The results are discussed in this section.

This apparatus was made from Perspex, which is inert to the chemicals used in the bleaching experiments. It was also transparent and this allowed for visual monitoring of the colour changes of the dye that was oxidised.

The cross flow apparatus is depicted schematically in Figure 192 and photographs of the actual apparatus are provided in Figures 193 and 196. It consists of two rectangular chambers cut into the top and bottom halves of the apparatus. The SCF sits between the two halves and when they are clamped together a water-tight seal is made via a rubber O-ring gasket. The hydrogen peroxide solution sits in one chamber and the dye solution is slowly pumped through the other chamber by a peristaltic pump. A small hydrostatic head of pressure causes the hydrogen peroxide to slowly permeate through the SCF as the dye solution flows across the other side of the SCF, but this solution is not under any
pressure. On the hydrogen peroxide side of the SCF, support for the film is provided by an acrylic insert that allows the hydrogen peroxide to contact all of the SCF surface. On the dye or substrate side of the SCF a chemical-resistant mesh is present that sits on top of the SCF and gently presses the film onto the support below in the hydrogen peroxide. The mesh creates turbulence within the flowing substrate solution so that rapid mixing of the solution and rapid localised flow occurs across the surface of the SCF.
Figure 192: Schematic diagram part by part in small cross-flow device
Figure 193: Schematic diagram of small cross-flow
The whole set up including peristaltic pump and hydrogen peroxide reservoir is shown in Figure 195.

Figure 194: Actual image of small cross-flow

Figure 195: The whole set up including peristaltic pump and hydrogen peroxide reservoir
Two very similar cross-flow units were manufactured, one with chambers (9 x 4 x 0.3) cm and the other with larger chambers, (19 x 3 x 0.3) cm.

Figure 196: Schematic diagram of the large cross-flow

Figure 197: Peroxide support on the bottom reservoir
Mesh

The function of the mesh was to create turbulence within the solution as it flowed through the chamber in the cross-flow apparatus. Three difference “generations” of the mesh were designed and produced with the aim of providing ever greater turbulence in the flow of the solution. Each new ‘generation’ of the mesh was re-designed to improve the previous ‘generation’ of mesh. Images of all three mesh designs in sequence are shown in Figures 198-201.
Figure 198: Schematic diagram of the first generation mesh

Figure 199: Actual picture of the first generation mesh
Figure 200: Schematic diagram of the second generation mesh
Figure 201: Schematic diagram of the third generation mesh
The meshes were all produced using a 3D printer and illustrated here using CAD exchanger (acknowledgement to University of Auckland technical services)

**Preliminary experiments carried out using the small cross-flow apparatus**

Initial experiments were carried out using the first generation mesh and without the $\text{H}_2\text{O}_2$ acrylic support in the hydrogen peroxide solution. When present, this acrylic support allowed the hydrogen peroxide to flow into the device from the reservoir and contact the SCF as well as supporting the membrane.

The conditions used for the first experiments are summarised in Table 70. The results are present in Table 71.

**Summarize dye bleaching using first generation cross flow**

<table>
<thead>
<tr>
<th>Catalyst: FeB* Dye moles ratio</th>
<th>Orange II 1.0 μmoles in 20 mL</th>
<th>$\text{H}_2\text{O}_2$ 200.0 μmoles in 200 mL</th>
<th>Flow rate 1.0 mL/min</th>
<th>Height of reservoir above the device 20.0 cm</th>
<th>pH 9.5 on Orange II side and pH 10.5 on $\text{H}_2\text{O}_2$</th>
<th>Dimension of cross-flow (9 x 4 x 0.3) cm</th>
<th>Mesh First generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:1</td>
<td>10.0 μmoles</td>
<td>1.0 mL/min</td>
<td>20.0 cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 70: Bleaching condition in cross-flow (10:1) mole ratio of FeB*: Orange (II) at pH 9.5 x 10.5 at flow rate 1.0 mL/min with first generation mesh*

<table>
<thead>
<tr>
<th>Substrate solution</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entering cross-flow apparatus</td>
<td>1.153</td>
</tr>
<tr>
<td>Exiting cross-flow apparatus</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Table 71: Bleaching result of first bleaching with first generation mesh*
The initial absorbance of the dye solution was 1.15. After one chamber volume of dye solution (11.0 mL) had flowed through the apparatus, the absorbance of the exiting, bleached dye solution was only 0.10. This showed that the SCF could be successfully used in this type of configuration. In this reaction there were 10 µmole of catalyst (FeB*) on the SCF and 1 µmole of dye per mL of solution. The chamber volume was 20.0 mL. The initial absorbance of the dye solution was 1.15. Under these conditions, if the flow rate was maintained at 1.0 mL/min the orange (II) dye solution exiting the apparatus after one chamber volume (11.0 mL) had flowed through it had an absorbance of 0.10. This showed that the SCF could be successfully used in this type of configuration.

Preliminary reactions were also done using the dye pinacyanol chloride. The conditions used are collected in Table 7. In the first experiment the pH of the dye solution was 9.5 and the pH of the hydrogen peroxide solution was 10.5. With a flow rate of 3.0 mL/minute, the exiting dye solution after one chamber volume had passed through (11.0 mL) the absorbance of the exiting, bleached dye solution was only 0.13. In the second experiment where the pH of the dye solution was 7.0 and the pH of the hydrogen peroxide solution was 10.5. With a flow rate of 1.0 mL/minute, the exiting dye solution after one chamber volume had passed through (11.0 mL) the absorbance of the exiting, bleached dye solution was only 0.15.
<table>
<thead>
<tr>
<th>Condition</th>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>PCl</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH</th>
<th>Dimension of cross-flow</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCI A</td>
<td>10:1 10.0 µmoles in 20 mL</td>
<td>1.0 µmoles in 200 mL</td>
<td>200.0µmoles in 200 mL</td>
<td>3.0 mL/min</td>
<td>20.0 cm</td>
<td>9.5 on PCl side and pH 10.5 on H₂O₂</td>
<td>(9 x 4 x 0.3) cm</td>
<td>First generation</td>
<td></td>
</tr>
<tr>
<td>PCI B</td>
<td>10:1 10.0 µmoles in 20 mL</td>
<td>1.0 µmoles in 200 mL</td>
<td>200.0µmoles in 200 mL</td>
<td>1.0 mL/min</td>
<td>20.0 cm</td>
<td>7.0 on PCl side and pH 10.5 on H₂O₂</td>
<td>(9 x 4 x 0.3) cm</td>
<td>First generation</td>
<td></td>
</tr>
</tbody>
</table>

Table 72: Bleaching condition in cross-flow (10:1) mole ratio of FeB*: PCI with first generation mesh
All these experiments were done with no hydrogen peroxide support with the first generation membrane, hence the results obtained here could be improved further. Before discussing further the different conditions that will be used, bleaching reaction times were first monitored to see if there would be any difference in using a different mesh design. The first blank experiment was performed to show the important of mesh to create turbulence and different mesh design that could improve the turbulence and eventually find the optimum condition with almost complete bleaching at fast flow rate. The results and conditions are shown below (new insert and support):

From the experiments carried out in the beakers and in the U-tube apparatus, it was well established that stirring rate was an important parameter in determining the rate of oxidation. It was therefore expected that generating turbulence in the dye solution as it flowed over the SCF would probably also increase the rate of oxidation of the dye. Experiments were therefore carried out to explore this idea. Oxidation reactions with either no mesh present in the chamber containing the dye, or different types of mesh were performed and the results compared. To obtain information about how fast the dye solution was oxidised in each case, the absorbance of the dye solution exiting the cross-flow apparatus was measured for a range of different flow rates. The general conditions used for the experiments involving the oxidation of orange II are listed in Table 73. After 20 mL solution exiting cross-flow apparatus, approximately 1 mg/L hydrogen peroxide can be detected using hydrogen peroxide test strip.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Dimension of cross-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>140:1</td>
<td>140.0 µmoles in 20 mL</td>
<td>1.0 µmoles in 200 mL</td>
<td>200.0 µmoles in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>20.0 cm</td>
<td>(I) = 7</td>
<td>(F)= 9.5</td>
<td>(I) =11.0</td>
</tr>
</tbody>
</table>

Table 73: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min.
In the first experiment there was no mesh present in the dye chamber and so minimal turbulence would be expected as the dye flowed through the chamber. The absorbance of the exiting solution as the flow rate was increased from 1.0 mL/minute to 10 mL/minute is given in Figure 202.

For each flow rate value, 20 mL of the orange (II) solution was passed through the apparatus before the final absorbance was measured. The volume of solution contained within the chamber was ca. 7.0 mL. The results showed that without any mesh present the absorbance of the exiting solution steadily rose until at 10 mL/minute very little bleaching of the dye occurred at all.

The experiment was then repeated with the first generation mesh present in the dye chamber. This mesh had a simple net structure as shown in Figure 198. The absorbance of the exiting solution as the flow rate increased is presented in Figure 203. The presence of the mesh improved the performance with the absorbance of the exiting solution only rising above 0.2 as the flow rate increased above 4 mL/minute (cf absorbance was 0.45 at 4 mL/minute with no mesh). At 10 mL/minute the absorbance rose to 0.8.

The same experiment was then carried out using a second generation mesh in the dye chamber. This mesh was designed to give a more contorted flow path and hence generate more turbulence. The results presented in Figure 205 show a very significant improvement in
performance. Even with a flow rate of 5 mL/minute, the absorbance of the exiting solution was less than 0.1. At a flow rate of 10 mL/minute the absorbance rose to 0.7.

To show that the designed contorted flow path was responsible for this very significant improvement in performance, the experiment with the second generation mesh was repeated, but it was placed into the chamber upside down. The SCF was then contacted by the solid cross-members of the mesh, rather than by the open curved features. The results are presented in Figure 204. The performance is much degraded. It is worse than that with the first generation mesh present and is rather similar to when no mesh was present at all.

To see what effect adsorbing a larger amount of catalyst on the SCF would have, a bleaching experiment was carried out with 140 µmole of adsorbed catalyst. The conditions for the reaction are summarised in Table 78 and the results presented in Figure 206. This resulted in another big step up in performance, with the absorbance of the exiting solution less than 0.1 until a flow rate of 7.5 mL/minute is exceeded. Even at a flow rate of 10 mL/minute the absorbance of the exiting solution was only 0.45. These results very clearly demonstrate how performance of the SCFs in the cross-flow configuration can be enhanced through improved mesh design and by increasing the amount of adsorbed catalyst.
<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB* µmoles</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Dimension of cross-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>140:1</td>
<td>140.0 µmoles</td>
<td>1.0 µmole in 20 mL</td>
<td>200.0 µmole in 200 mL</td>
<td>(1.0–10.0) mL/min</td>
<td>20.0 cm</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
<td>(9 x 4 x 0.3) cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 8.1</td>
<td>(F) = 11.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 74: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with first generation mesh. (1mg/L hydrogen peroxide can be detected pass through using peroxide test strip)

![Plot of Absorbance vs time for bleaching in cross flow for FeB* and Orange (II), 140:1 ratio pH 7 x 11 first generation mesh](image)

Figure 203: Plot of absorbance vs time for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with first generation mesh
Table 75: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with second generation upside down

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB* µmole in 20 mL</th>
<th>Orange II µmole in 200 mL</th>
<th>H₂O₂ mL/min</th>
<th>Flow rate (1.0-10.0) mL/min</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Dimension of cross-flow (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140:1</td>
<td>140.0</td>
<td>1.0</td>
<td>200.0</td>
<td>(1.0-10.0)</td>
<td>20.0</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
<td>(9 x 4 x 0.3)</td>
</tr>
<tr>
<td></td>
<td>µmole</td>
<td>µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 204: Plot of absorbance vs time for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with second generation mesh upside down
<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB* µmoles</th>
<th>Orange II µmoles</th>
<th>H2O2 µmoles</th>
<th>Flow rate mL/min</th>
<th>Height of reservoir above the device cm</th>
<th>pH Orange II side (I)</th>
<th>pH peroxide side (F)</th>
<th>Dimension of cross-flow (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140:1</td>
<td>140.0 µmoles</td>
<td>1.0 µmoles in 20 mL</td>
<td>200.0 µmoles in 200 mL</td>
<td>(1.0-10.0)</td>
<td>20.0</td>
<td>7.0</td>
<td>8.0</td>
<td>(9 x 4 x 0.3)</td>
</tr>
</tbody>
</table>

Table 76: Bleaching condition in cross-flow (10:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with second generation

![Absorbance vs time for cross flow bleaching with FeB* and Orange (II) ratio 10:1 at pH 7 x 11.](image)

Figure 205: Plot of absorbance vs time for (140:1) mole ratio at pH 7 and pH 11, 1.0 mM H2O2 with flow rate from 1.0 to 10.0 mL/min with second generation mesh
Having established the importance of the amount of adsorbed catalyst on the SCFs, the performance of films containing different amounts of catalyst under these conditions was investigated further. The conditions used for the experiments are summarised in Table 77. The amount of catalyst present on the different SCFs varied from 1.0 µmole to 140.0 µmole using smaller cross-flow (9 x 4 x 0.3) cm. A second generation mesh was used for all these experiments. The results obtained are presented in Figure 206. It can be seen that as the number of moles of catalyst on the SCF increases, so the performance increases with the best results obtained with the largest catalyst loading (140 µmoles). There is no sign therefore that under these conditions further increases in catalyst loading would not result in further increases in performance of the SCF in this configuration.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1.0 µmole</td>
<td>1.0 µmole in 20 mL</td>
<td>200.0 µmole in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>20.0 cm</td>
<td>(I) = 7</td>
<td>(I) =11.0</td>
</tr>
<tr>
<td>10:1</td>
<td>10.0 µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:1</td>
<td>20.0 µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50:1</td>
<td>50.0 µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80:1</td>
<td>80.0 µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100:1</td>
<td>100.0 µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140:1</td>
<td>140.0 µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 77: Bleaching condition in cross-flow using (1:1) to (140:1) mole ratio of FeB*: Orange (II) with flow rate range from (1.0-10.0) mL/min with second generation mesh
From the data in Figure 206, a plot of flow rate at which absorbance rises above 0.2 (breakthrough flow point) vs amount of catalyst on the SCF can be generated. This is shown in Figure 207. This graphically illustrates that performance generally improves as the amount of catalyst on the SCF increases.

Figure 206: Plot of absorbance vs time for different range of mole ratio at pH 7 and pH 11, 1.0 mM H₂O₂ with flow rate from 1.0 to 10.0 mL/min with second generation mesh

Figure 207: Plot of catalyst to dye mole ratio vs breakthrough flow rate point
Having established that under the conditions used above the SCF in the cross-flow apparatus could oxidise dye solutions quite rapidly, attempts were then made to estimate how long the catalyst might last under these conditions and whether the lifetime could be improved. Since small amounts of hydrogen peroxide (approximately 1ppm) were detected in the exiting dye solution from the above experiments it was clear that too much of the hydrogen peroxide solution was permeating through the SCF. As it is known that excess hydrogen peroxide can cause destruction of the FeB* catalyst both in homogeneous solution and when it is anchored onto the SCF, attempts were made to limit the hydrogen peroxide used. To do this two experiments were carried out, one with the hydrogen peroxide reservoir held 40 cm above the cross-flow apparatus and one with the height at 20 cm. The flow rate was set at 5.0 mL/minute and the absorbance of the exiting solution was monitored with time. The conditions for the experiments are given in Table 78 and the results are presented in Figure 208.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH hydrogen peroxide side</th>
<th>Dimension of cross-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140:1</td>
<td>7 x 10⁻⁴</td>
<td>5 x 10⁻⁶</td>
<td>200 µmoles in 200 mL</td>
<td>5.0 mL/min</td>
<td>20.0 cm</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
<td>(9 x 4 x 0.3) cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 11.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>140:1</td>
<td>7 x 10⁻⁴</td>
<td>5 x 10⁻⁶</td>
<td>200 µmoles in 200 mL</td>
<td>5.0 mL/min</td>
<td>40.0 cm</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
<td>(9 x 4 x 0.3) cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 11.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 78: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: Orange (II) with flow rate range from 5.0 mL/min with second generation mesh with hydrogen peroxide reservoir 20.0 and 40.0 cm
The results showed that using a lower reservoir height resulted in slightly more of the dye being bleached. Hence, by reducing the amount of hydrogen peroxide that permeates the SCF, the performance of the SCF could be improved.

Bleaching of the dye pinacyanol chloride using the cross-flow apparatus was also investigated as a function of flow rate. Conditions that were used for these experiments are summarised in Table 79 and the height of the hydrogen peroxide reservoir was (20 and 40) cm above the apparatus. Plots of absorbance of the exiting solution vs flow rate for catalyst loadings of 140 µmole are presented in Figures 209 and 210, respectively. For the lower loading of 80 µmole the absorbance of the exiting solution rose rapidly above 0.1 as the flow rate exceeded 5.5 mL/minute (Figure 209). For the corresponding experiment with orange II this occurred at a flow rate of about 3.5 mL/minute. For the higher catalyst loading of 140 µmole the absorbance of the exiting solution rose rapidly above 0.1 as the flow rate exceeded about 7.5 mL/minute (Figure 210). For the corresponding experiment with orange II this also occurred at a flow rate of about 7.5 mL/minute. As with the experiments with the SCFs in the beakers and in the U-tubes, this indicates that the rate-limiting step is a process other than the oxidation of the dye by the catalyst.

![Figure 208: Plot of absorbance vs time for (140:1) mole ratio at pH 7x11, 1.0 mM H₂O₂ with flow rate from 5.0 mL/min with second generation mesh and hydrogen peroxide reservoir height (20-40) cm](image-url)
<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>PCl</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Dimension of cross-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>80:1</td>
<td>80.0</td>
<td>1.0 µmole in 20 mL</td>
<td>200.0 µmole in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>20.0 cm</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
<td>(9 x 4 x 0.3) cm</td>
</tr>
<tr>
<td></td>
<td>µmole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 8.0</td>
<td>(F) = 11.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 79: Bleaching condition in cross-flow (80:1) mole ratio of FeB*: PCl with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm

![Absorbance vs time for cross flow bleaching with FeB* and Pinacyanol Chloride ratio 80:1 at pH 7 x11](image)

Figure 209: Plot of absorbance vs time for (80:1) mole ratio at pH 7 and 11, 1.0 mM H₂O₂ with flow rate from (1.0-10.0) mL/min with second generation mesh
Table 80: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCl with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB* (µmoles in 20 mL)</th>
<th>PCl (µmoles in 200 mL)</th>
<th>Flow rate (1.0-10.0) mL/min</th>
<th>Height of reservoir above the device (20.0 cm)</th>
<th>pH Orange II side (I) = 7</th>
<th>pH peroxide side (F) = 8.0</th>
<th>Dimension of cross-flow (9 x 4 x 0.3) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>140:1</td>
<td>140.0 µmoles</td>
<td>1.0 µmoles</td>
<td>200.0 µmoles</td>
<td>(I) = 7</td>
<td>(F) = 8.0</td>
<td></td>
<td>(9 x 4 x 0.3) cm</td>
</tr>
</tbody>
</table>

Figure 210: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCl with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm
Given the positive results obtained when the hydrogen peroxide reservoir height was reduced to 20 cm, the effects of reduction to the concentration of the hydrogen peroxide solution on catalyst lifetime were investigated. This was done by changing the concentration of hydrogen peroxide from 1.0 mM to 0.1 mM, and observing any significant changes that occurred in the plot of absorbance vs volume of dye when the height of the reservoir was held at 20 cm or 40 cm. The reaction conditions are given in Table 81 and the results are given in Figures 211 and 212 respectively.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>PCI</th>
<th>H₂O₂</th>
<th>Flow rate (mL/min)</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140:1</td>
<td>0.7 mmole</td>
<td>5.0 μmole in 100 mL</td>
<td>20.0 μmole in 200 mL</td>
<td>5.0</td>
<td>20.0 cm</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 11.0</td>
</tr>
<tr>
<td>2</td>
<td>140:1</td>
<td>0.7 mmole</td>
<td>5.0 μmole in 100 mL</td>
<td>20.0 μmole in 200 mL</td>
<td>5.0</td>
<td>40.0 cm</td>
<td>(I) = 7</td>
<td>(I) = 11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 11.0</td>
</tr>
</tbody>
</table>

Table 81: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCI with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm

Figure 211: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCI with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm and 0.1 mM H₂O₂
The results did not show much improvement compared with those obtained.

![Graph](image-url)

**Figure 212**: Bleaching condition in cross-flow (140:1) mole ratio of FeB*: PCI with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 40.0 cm and 0.1 mM H₂O₂.

There was very little difference in the performance of the SCFs when these changes were made and so under these conditions reducing the concentration of the hydrogen peroxide does not improve performance very much. However, reducing this concentration by a factor of ten would result in overall reduced consumption of hydrogen peroxide.

To demonstrate that other catalysts can be used on the SCFs in this cross-flow apparatus, some experiments with FeB\(^{1}\) were carried out. Using the conditions summarised in Table 83, the absorbance of the exiting dye solution was monitored with volume when a constant flow rate of 5 mL/minute was used. The results are presented in Figure 213. The results were very similar to those obtained with FeB\(^{*}\), showing that this catalyst also performs well with the SCF this configuration. Reduction of the hydrogen peroxide concentration to 0.1 mol L\(^{-1}\) did not significantly reduce the performance (see Figure 213), as was observed for FeB\(^{*}\).
<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB$^1$</th>
<th>Orange II</th>
<th>H$_2$O$_2$</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Dimension of cross-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>140:1</td>
<td>0.7 mmole</td>
<td>5.0 µmole in 100 mL</td>
<td>20 µmole in 200 mL</td>
<td>5.0 mL/min</td>
<td>40.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 11.0</td>
<td>(9 x 4 x 0.3) cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 82: Bleaching condition in cross-flow (140:1) mole ratio of FeB$^1$ Orange II with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 20.0 cm

![Absorbance vs volume](chart.png)

Figure 213: Plot of bleaching in cross-flow (140:1) mole ratio of FeB$^1$ Orange II with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 40.0 cm and 0.1 mM H$_2$O$_2$
3.4.1 Large cross-flow

In an attempt to improve performance a new cross-flow apparatus was designed and built. The dimensions of the chambers were changed to $19 \times 3 \times 0.3$ cm so that they became longer and slightly narrower than in the original apparatus. As a result the chambers had a larger volume (17 mL). The aim of the change was to increase the velocity of the flow across the film surface (and hence the turbulence) for a given flow rate and to also give the SCF longer to interact with the dye solution before it exited. It was expected that this would allow higher flow rates to be used for a given level of bleaching. For the first experiment using the larger cross-flow apparatus the conditions in Table 83 were used.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB(^{1})</th>
<th>Orange II</th>
<th>H(_2)O(_2)</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Dimension of cross-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>80:1</td>
<td>80.0 (\mu)mole</td>
<td>1.0 (\mu)mole</td>
<td>200 (\mu)mole in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>(19 x 3 x 0.3) cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 9.5</td>
</tr>
</tbody>
</table>

Table 83: Bleaching condition in cross-flow (80:1) mole ratio of FeB\(^{1}\): Orange II with flow rate range from 5.0 mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm
A mesh of second generation design was used and the height of the reservoir above the apparatus was 30 cm.

The results showed that at a flow rate of approximately 5 mL/min, the dye was mostly bleached but with increasing flow rate the absorbance of the exiting solution rose and was to 0.4 at 10 mL/minute. Overall this was a similar performance to that obtained for the shorter apparatus with 140 µmole of adsorbed catalyst (see Figure 208).

From the results obtained with the shorter apparatus either with no mesh, a first generation mesh or a second generation mesh, it was clear that the mesh design was a very important factor in the performance of the SCF in the cross-flow apparatus. Therefore a modified version of the second generation mesh was designed with the cross-members placed closer together and the “arched” cut-out parts made slightly smaller. The aim was that this would make the flow even more turbulent. A bleaching experiment was performed with this third generation mesh in the dye chamber. The conditions used are given in Table 84 and the results are presented in Figure 215.
<table>
<thead>
<tr>
<th>Condition</th>
<th>Catalyst: Dye moles ratio</th>
<th>FeB(^1) µmoles</th>
<th>Orange II µmole</th>
<th>H(_2)O(_2) 200.0µmoles in 200 mL</th>
<th>Flow rate (1.0-10.0) mL/min</th>
<th>Height of reservoir above the device 30.0 cm</th>
<th>pH Orange II side (I) = 7.0</th>
<th>pH peroxide side (I) = 9.5</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80:1</td>
<td>80.0 µmoles</td>
<td>1.0 µmole</td>
<td>(1.0-10.0) mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>Second generation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 7.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>80:1</td>
<td>80.0 µmoles</td>
<td>1.0 µmole</td>
<td>(1.0-10.0) mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>Third generation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 7.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 84: Bleaching condition in cross-flow (80:1) mole ratio of FeB\(^1\): Orange II with flow rate range from (1.0-10.0) mL/min with second and third generation mesh hydrogen peroxide reservoir 30.0 cm

![Plot of Absorbance vs flow rate for Orange (II), 80:1 moles ratio pH 7x 9.5 surface area (19 x 3 x 0.3 cm) with second and third generation mesh, 1.0 mM H\(_2\)O\(_2\)](image)

Figure 215: Plot of bleaching in cross-flow (80:1) mole ratio of FeB\(^1\): Orange II with flow rate range from (1.0-10.0) mL/min with second and third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H\(_2\)O\(_2\)
This result showed that the new mesh did improve the performance slightly, with more dye being bleached at all flow rates measured. This illustrates that further improvements in performance might be obtained with further changes to the mesh design, but this was not investigated further in this study. In addition attempts were made to increase the catalyst loading with the hope that in doing so complete bleaching of the dye would occur at the fastest flow rate tested. 160 µmole of FeB* was adsorbed onto the SCF and the other conditions used for this experiment are shown in Table 85 and the results are presented in Figures 216.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>160:1</td>
<td>160.0 µmoles</td>
<td>1.0 µmole</td>
<td>200.0µmoles in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) =9.5</td>
<td>Third generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 9.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 85: Bleaching condition in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm.

Figure 216: Plot of bleaching in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂.
The results showed that most of the Orange (II) dye was bleached, even using the highest flow rate available of 10 mL/min. At lower flow rates the dye was essentially completely bleached. Following this very positive result, an experiment was carried out with the hydrogen peroxide solution buffered at pH 11.0 since this is the pH where the FeB* catalyst operates at the highest rate. The conditions used are given in Table 86 and the results are presented in Figure 217.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>160:1</td>
<td>160.0 µmole</td>
<td>1.0 µmole</td>
<td>200.0 µmoles in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) =11.0</td>
<td>Third generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F)= 11.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 86: Bleaching condition in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm at pH 7x11.

Figure 217: Plot of bleaching in cross-flow (160:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂
There was no clear improvement in performance at all when the hydrogen peroxide solution was at the higher value of pH 11.0. This indicated that the rate of oxidation of the dye by the catalyst was not the rate-limiting step in the bleaching here. The same bleaching experiment was then carried out using a second generation mesh to see whether the performance would be inferior (conditions summarised in Table 87). The results presented in Figure 218 show that under these conditions there was very little difference in the performance of the two meshes, except that possibly the third generation mesh performed slightly better at the highest flow rate, possibly as a result of increased turbulence.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB⁺</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>160:1</td>
<td>160.0 µmole</td>
<td>1.0 µmole</td>
<td>200.0 µmole in 200 mL</td>
<td>(1.0-10.0) mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 11.0</td>
<td>Second generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 11.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 87: Bleaching condition in cross-flow (160:1) mole ratio of FeB⁺: Orange II with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm at pH 7x11.
Figure 218: Plot of bleaching in cross-flow (160:1) mole ratio of FeB\(^{2+}\): Orange II with flow rate range from (1.0-10.0) mL/min with second generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H\(_2\)O\(_2\)
Having demonstrated that the larger cross-flow apparatus with the third generation mesh, 160 µmole of FeB* on the SCF, performed very well in bleaching the dye solution at the highest flow rates available (10 mL/minute) attempts were made to estimate the catalyst lifetime and the amount of dye that could be bleached before the catalyst degraded. To do this, 500 mL of Orange (II) dye were passed through the cross-flow apparatus at 10 mL/minute under the conditions in Table 88.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>280:1</td>
<td>0.7 mmole</td>
<td>2.5 µmole</td>
<td>200.0 µmole in 200 mL</td>
<td>10.0 mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>third generation</td>
</tr>
</tbody>
</table>

Table 88: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from (1.0-10.0) mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm at pH 7x9.5

![Absorbance vs volume for (240:1) FeB* to Orange (II), pH 9.5 x 7, at flow rate 10 mL/min, height 30-35 cm, third generation mesh, 1.0 mM H₂O₂](image)

Figure 219: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂
This result are given in Figure 219 and show that under these conditions the efficiency of the SCF in catalysing the bleaching of the dye slowly drops off as more dye solution is passed through. After 500 mL, the absorbance of the exiting solution was 0.7, indicating that only about 30% of the dye was being bleached at that point. From results obtained previously, it was suspected that the reason for the reduction in catalyst activity was that the catalyst was being exposed to a high concentration of hydrogen peroxide over the 50 minute period of the reaction and this was responsible for degrading a significant amount of the catalyst. In an attempt to reduce this problem, the concentration of the hydrogen peroxide was reduced by a factor of ten to 0.10 mol L⁻¹. The other conditions used were the same as those in the above experiment and the results are given in Table 89. The results clearly showed that reducing the hydrogen peroxide concentration significantly improved the performance with the absorbance of the exiting solution only 0.5 after 500.0 mL orange II solution was passed through.

![Plot of Absorbance vs volume (mL) for (280:1) FeB⁺ to Orange II, pH 9.5 and pH 7.0 at flow rate 10mL/min, height 30 cm, third generation mesh, 0.1 mM H₂O₂](image)

Figure 220: Plot of bleaching in cross-flow (280:1) mole ratio of FeB⁺: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 1.0 mM H₂O₂
This result showed that about 300 mL of the Orange (II) solution could be bleached using 0.1 mM H$_2$O$_2$ compared to the 200 mL that was bleached when using 1 mM H$_2$O$_2$. This demonstrated a great improvement in the bleaching of the orange II dye. Since many of the actual pollutants that are found in contaminated waters are present in ppm to ppb quantities, the concentration of the orange (II) dye was then lowered so that it was somewhat closer to this real situation. The conditions that were chosen are shown in Table 89. The results presented in Figure 221 clearly show that in terms of the percentage of the total amount of dye in solution that was bleached there was a clear improvement. Thus after passing 200 mL of solution the absorbance was 0.01 (cf. 0.3 for the previous experiment) and after passing 500 mL the absorbance was 0.045 (cf. 0.7 for the previous experiment). However, in terms of the total number of moles of dye bleached, less was bleached with this more dilute solution.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB$^*$</th>
<th>Orange II</th>
<th>H$_2$O$_2$</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>280:1</td>
<td>0.7 mmole</td>
<td>2.5 µmole in 200 mL</td>
<td>10.0 mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>third generation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 9.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 89: Bleaching condition in cross-flow (280:1) mole ratio of FeB$^*$: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.1 mM H$_2$O$_2$ at pH 7x9.5

![Absorbance vs volume (mL) for (280:1) FeB$^*$ to Orange (II) pH 9.5 and pH 7, at flow rate 10 mL/min, height 30.0 cm, third generation mesh,0.1 mM H$_2$O$_2$,](image)

Figure 221: Plot of bleaching in cross-flow (280:1) mole ratio of FeB$^*$: Orange II with flow rate range from 10.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.1 mM H$_2$O$_2$
In a further attempt to improve the catalyst lifetime, the concentration of the hydrogen peroxide was reduced even further. Another bleaching experiment was carried out using a hydrogen peroxide concentration of 0.01 mol L\(^{-1}\) and buffered at pH 9.5. In this way the rate of catalyst activation should be much slower and so catalyst molecules should not be in the activated form so long before they react with a dye molecule. Since it was expected that the rate of oxidation would be reduced under these conditions the flow rate through the apparatus was reduced to 5 mL/minute. The other conditions used are listed in Table 90 and the results are presented in Figure 222. These changes did indeed lead to an improvement of performance. After passing 500 mL of solution the absorbance was only 0.02 (cf 0.045 when 0.10 mol L\(^{-1}\) hydrogen peroxide was used, Figure 222) and after 1000 mL it was 0.07 (cf 0.08 when 0.10 mol L\(^{-1}\) hydrogen peroxide was used).

<table>
<thead>
<tr>
<th>Catalyst: Dye moles</th>
<th>FeB(^{\ast})</th>
<th>Orange II</th>
<th>H(_2)O(_2)</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>280:1</td>
<td>0.7</td>
<td>2.5 µmole</td>
<td>2.0 µmole in 200 mL</td>
<td>5.0 mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 9.5</td>
<td>third generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.9</td>
<td>(F) = 9.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 90: Bleaching condition in cross-flow (280:1) mole ratio of FeB\(^{\ast}\): Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.01 mM H\(_2\)O\(_2\) at pH 7 \& 9.5

![Absorbance vs volume for (280:1) FeB\(^{\ast}\) to Orange (II), pH (9.5 and 7), at flow rate 5 mL/min, height 30.0 cm, third generation mesh, 0.01 mM H\(_2\)O\(_2\) ](image)

Figure 222: Plot of bleaching in cross-flow (280:1) mole ratio of FeB\(^{\ast}\): Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.1 mM H\(_2\)O\(_2\)
In yet another attempt to improve performance an experiment were carried out using the hydrogen peroxide buffered at the lower pH of 8.0. It was reasoned that in lowering the pH further, the rate of catalyst deactivation would be further reduced leading ultimately to less catalyst degradation. An experiment was first performed with the hydrogen peroxide concentration at 0.1 mol L\(^{-1}\) (full conditions given in Table 91) but as the results in Figure 223 showed no real improvement over the results obtained when the hydrogen peroxide was at this same concentration and buffered at pH 9.5 (see Figure 222). An additional experiment was then carried out in which the hydrogen peroxide was buffered at pH 8.5 and had a concentration of 0.01 mol L\(^{-1}\). The conditions are listed in Table 92 and the results are presented in Figure 224.

<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB(^{\circ})</th>
<th>Orange II</th>
<th>H(_2)O(_2)</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>280:1</td>
<td>0.7 mmole</td>
<td>2.5 µmole</td>
<td>20.0µmole in 200 mL</td>
<td>5.0 mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 8.0</td>
<td>third generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.3</td>
<td>(F) = 8.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 91: Bleaching condition in cross-flow (280:1) mole ratio of FeB\(^{\circ}\): Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.1 mM H\(_2\)O\(_2\) at pH 7x8.0

![Absorbance vs volume for 2x (140:1) FeB\(^{\circ}\) to Orange (II), pH (8 and 7), at flow rate 5mL/min, height 30-35 cm, new mesh big cross flow, 0.1 mM H\(_2\)O\(_2\).](image)

Figure 223: Plot of bleaching in cross-flow (280:1) mole ratio of FeB\(^{\circ}\): Orange II with flow rate 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.1 mM H\(_2\)O\(_2\).
<table>
<thead>
<tr>
<th>Catalyst: Dye moles ratio</th>
<th>FeB*</th>
<th>Orange II</th>
<th>H₂O₂</th>
<th>Flow rate</th>
<th>Height of reservoir above the device</th>
<th>pH Orange II side</th>
<th>pH peroxide side</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>280:1 0.7 mmole</td>
<td>2.5 µmole</td>
<td>2.0 µmole in 200 mL</td>
<td>5.0 mL/min</td>
<td>30.0 cm</td>
<td>(I) = 7.0</td>
<td>(I) = 8.5</td>
<td>third generation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(F) = 7.5</td>
<td>(F) = 8.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 92: Bleaching condition in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate range from 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm, 0.01 mM H₂O₂ at pH 7 and pH 8.5

![Absorbance vs volume](image)

Figure 224: Plot of bleaching in cross-flow (280:1) mole ratio of FeB*: Orange II with flow rate 5.0 mL/min with third generation mesh hydrogen peroxide reservoir 30.0 cm and 0.01 mM H₂O₂, at pH 7 and pH 8.5
It is clear that under these conditions the performance of the SCF containing the FeB\(^*\) catalyst was dramatically improved. After passing 500 mL of solution most of the dye was bleached (absorbance of exiting solution 0.01) and after passing 1000 mL (which took a time of 3 hour 20 minutes) the absorbance was only 0.035. Clearly the bleaching performance was much better than under the previous conditions used (see Figures 222 and 223). These results strongly suggest that using hydrogen peroxide at very low concentration and at low pH is beneficial for improving the catalyst lifetime while still allowing the SCF to catalyse the oxidation of substrate dye at a reasonably fast rate. It is proposed that these changes reduced the rate of catalyst activation and this in turn led to an increase in catalyst lifetime.

3.4.2 Conclusions for the Cross flow experiments

Preliminary experiments using SCFs in a cross-flow apparatus showed that in this configuration the SCFs could successfully catalyse the bleaching of dye solutions using basic hydrogen peroxide solution that was separated from the dye solutions by the SCF. The bleaching reactions were successful even when the pH of the dye solution was at the environmentally relevant value of 7.0.

The influence that a number of different parameters had on the bleaching reactions was investigated. Changes were made to the design of the mesh insets that were placed into the chamber of the cross-flow apparatus through which the dye solution flowed. The purpose of the meshes was to create turbulent flow and therefore increase the rate of delivery of the dye to the surface of the SCF. Three different meshes were designed and tested. From the results it was clear that mesh design had a big influence on the efficiency of operation of the SCF in the cross-flow apparatus, with each successive design improving performance.

The amount of catalyst adsorbed onto the SCF also changed the performance. Generally the more catalyst present, the faster the dye was bleached (i.e. faster flow rates could be used to achieve the same level of bleaching as the amount of catalyst increased). As was found with the experiments using beakers or the U-tube apparatus, different catalysts could also be used on the SCF in the cross-flow apparatus. Tests with FeB\(^J\) showed this catalyst performed in a very similar manner to FeB\(^*\).
Different dyes could also be bleached using a cross-flow configuration for the SCFs. Both the negatively charged Orange II and the positively charged pinacyanol chloride were successfully bleached. Under the same conditions, the maximum flow rates that could be achieved for each of these dye solutions before significant amounts of unbleached dye was present in the exiting solution was very similar. These results are very similar to those carried out with the SCFs in the beakers and in the U-tubes which further supports the conclusion that the rate-limiting step is a process other than the oxidation of the dye by the catalyst in these systems.

A larger cross-flow apparatus was constructed and tested. The chambers in this version were considerably longer and slightly narrower, so that the velocity of the dye solution across the SCF was increased for a given flow rate and the length of time the solution was in contact with the SCF was increased. These changes had the expected effects. Faster flow rates could be used while still achieving nearly complete bleaching.

Tests were also carried out to obtain information about how long the catalyst would remain active under the conditions used in the cross-flow apparatus. It was found that the initial conditions used resulted in much of the catalytic activity being lost (ca. 70-80% of the dye exited unbleached) after about one litre of dye solution had been passed through the apparatus. While studying ways to increase the time the catalyst remain active it was found that both the concentration and pH of the hydrogen peroxide solution had a very big influence on catalyst lifetime, as well as the rate at which the hydrogen peroxide solution permeated the SCF. Using very dilute hydrogen peroxide (0.01 mol L\(^{-1}\)) at a pH of 8.5 and with a moderately small hydrostatic head (30 cm) with the dye solution at pH 7.0, the best results were obtained. Under these conditions 65% of the dye entering the apparatus was still bleached after one litre of dye solution had been passed though it over a time of 3 hours 20 minutes. It is expected that further changes to the operational parameters of the cross-flow apparatus could result in more improvements to the performance of the SCFs in this configuration.
3.4.3 Experimental procedures

3.4.3.1 Preparation of solutions for standardization of thiosulfate and hydrogen peroxide

Preparation of 2.00 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution

Specific gravity of 98\% H\(_2\)SO\(_4\) solution recorded on the bottle label = 1.84 g mL\(^{-1}\). For 0.5 L of 2.00 mol L\(^{-1}\), the calculation is as below:

\[
\begin{align*}
\text{c} &= \frac{n}{v} \quad \text{hence} \quad n = cv = 2 \text{ mol L}^{-1} \times 0.5 \text{ L} = 1 \text{ moles} \\
\text{mass} &= n \times Mr = 1 \text{ moles} \times 98.07 \text{ g mol}^{-1} = 98.07 \\
98.07 \text{ g} / 1.84 \text{ g mL}^{-1} &= 53.2989 \text{ mL}
\end{align*}
\]

Thus ca. 53.3 mL of 98 \% H\(_2\)SO\(_4\) is required to make up 0.5 L of a 2.00 mol L\(^{-1}\) solution. H\(_2\)SO\(_4\) (53.3 ml) was measured carefully into a measuring cylinder and poured gently using Pasteur pipette in 250 ml beaker. Stirred the mixture slowly until all the sulfuric acid was completely transferred into the beaker. The solution was then transferred into a 500 mL volumetric flask before add the remaining de-ionized water up to the mark.

Figure 225: Photograph of bleaching using small cross flow under condition specified in table 78 for the first 50 mL.
3.4.2.2 Preparation of 0.100 mol L\(^{-1}\) Na\(_2\)S\(_2\)O\(_3\) solution

Solid Na\(_2\)S\(_2\)O\(_3\).5H\(_2\)O (\(M_r = 24.8186\)) was added to ca. 0.5 L water in a 1 L volumetric flask and shaken for a while until all the solid dissolved. Then after allowing the sample to stand for a few minutes, the solution was made up to 1.00 L with de-ionized water.

3.4.2.3 Preparation of 2\% w/v KI solution

KI (0.12047g) was weighed into a 0.100 L volumetric flask and ca. 50 mL of de-ionized water added to the flask. The flask was then shaken until all the KI have dissolved. After the solution allowed to standing for a few minutes, de-ionized water was added until it reached the mark. The volumetric flask was wrapped in aluminium foil to avoid photo-decomposition.

3.4.2.4 Preparation of 1.00 mol L\(^{-1}\) KI solution

KI (16.6003 g) was weighed into a 100 mL beaker and added to a 0.100 mL volumetric flask. De-ionized water ca. 50 mL was used to rinse the beaker at least 3 times. The flask was then shaken until all the KI had dissolved. After standing for a few minutes, the solution was made up to 0.100 L with de-ionized water and wrapped in Al foil to avoid any photo –decomposition.

3.4.2.5 Preparation of saturated ammonium molybdate, (NH\(_4\))\(_6\)M\(_{24}\)O\(_{74}\)4.4H\(_2\)O solution

Water (ca.200 mL) was boiled in a conical flask on a hot plate (with a boiling stick inside the conical flask) while being stirred using a magnetic stirrer bar. Solid ammonium molybdate was added to the water until the solution was saturated. The ammonium molybdate solution was then transferred into a screw-cap bottle and cooled to room temperature.

3.4.2.6 Preparation of 1\% w/v starch solution

Starch (ca. 2.500 g) was weighed out in conical flask before ca. 250 mL deionised water was added into the flask. The flask was then gradually stirred using a magnetic stirrer bar and heated slowly on a hot plate until the starch had dissolved. The solution was then cooled to ambient temperature and transferred to a 250 mL storage bottle. The starch solution was refrigerated at 4 °C when not being used.

3.4.2.7 Preparation of 5x10\(^{-5}\) mol L\(^{-1}\) [Na]\(_2\)[FeB\(^{\cdot}\)Cl] in buffer solution at pH ca 9.5 with 0.01 mol L\(^{-1}\) concentration.

[Na]\(_2\)[FeB\(^{\cdot}\)Cl] (1.26921 mg) was weighed into a glass vial and then transferred (with the vial being washed at least 3 times) into a 50 mL volumetric flask with buffer solution at pH 9.5. The solution was then made up to 50 mL with more buffer solution and protected from light with Al foil to avoid any photo-decomposition.
3.4.2.8 Preparation of 1.0 mmol L\(^{-1}\) orange (II) dye solution

Orange (II) dye (17.516 mg) was weighed into a glass vial and then transferred (with the vial being washed at least 3 times) into a 50 mL volumetric flask with de-ionized water. The solution was then made up to 50 mL with more de-ionized water and protected from light with Al foil to avoid any photo-decomposition.

3.4.2.9 Preparation of ca. 0.2 mol L\(^{-1}\) H\(_2\)O\(_2\) solution

10.00 mL of 35 % H\(_2\)O\(_2\) solution was pipetted (CARE) into a clean and dry 0.500 L volumetric flask and ca. 250 mL of de-ionized water was added to the flask. The solution was then shaken until the solutions were well mixed. The solution was then made up to 0.500 L with more water. Since H\(_2\)O\(_2\) slowly decomposes under light, the volumetric flask was wrapped with Al foil and stored in the dark. For safety reasons a stopper was not used, instead parafilm was stretched over the top of the neck. This was in case of pressure build up through decomposition of the hydrogen peroxide.

3.4.2.10 Preparation of 1% w/v starch solution

Starch (5.00 g) was weighed out into a 50 mL volumetric flask and ca. 25 mL de-ionized water was added to the flask. The flask was shaken for a while and warmed with sonication until the starch had essentially dissolved.

3.4.2.11 Standardisation of 0.100 mol L\(^{-1}\) Na\(_2\)S\(_2\)O\(_3\) solution

KIO\(_3\) solution (25.00 mL, 0.0187 mol L\(^{-1}\)) and KI solution (5 mL, 1.00 mol L\(^{-1}\)) were added together with 100 mL water in a 250 mL conical flask. H\(_2\)SO\(_4\) (10.00 mL, 2.00 mol L\(^{-1}\)) solution was added and the liberated iodine titrated to a pale straw colour with Na\(_2\)S\(_2\)O\(_3\) solution. At this point in the titration ca. 10 drops of 1% starch solution was added and the titration finished dropwise until the blue colour disappeared. The flask was allowed to stand for ca. 30 sec and further addition of Na\(_2\)S\(_2\)O\(_3\) was added upon appearance of a blue colour in the solution. This process was repeated 3 times, or as many times as needed until concordant results were obtained within 0.04 mL.

3.4.2.12 Standardization of H\(_2\)O\(_2\) solution

H\(_2\)O\(_2\) solution (5 mL, ca. 0.1984 mol L\(^{-1}\)) was pipetted into a clean 250 mL conical flask containing water (ca 100 mL), H\(_2\)SO\(_4\) solution (10.00 mL, 2.00 mol L\(^{-1}\)) and saturated ammonium molybdate solution (5-10 drops). KI solution (10.00 mL, 2%) was pipetted into the flask, and the liberated iodine titrated to a pale straw colour with standardized Na\(_2\)S\(_2\)O\(_3\) solution (0.100 mol L\(^{-1}\)). At this point in the titration ca. 10 drops of 1 % starch solution was added and
the titration finished dropwise until the blue colour disappeared. The flask was allowed to stand for ca. 30 s and further Na$_2$S$_2$O$_3$ added upon any appearance of a blue colour in the solution. This process was repeated 3 times, or as many times as necessary until consistent result was achieved within 0.04 mL.$^{221}$

3.4.2.13 Standardization of H$_2$O$_2$ using a UV-VIS instrument

30% reagent grade hydrogen peroxide stock solution was obtained and diluted to produce (ca. 1%) H$_2$O$_2$ solution in a 250 mL volumetric flask. The solution was then covered with Al foil to prevent any possibility of photo-induced degradation. The 1% H$_2$O$_2$ stock solution (1.00 mL) was pipetted into a 20 mL volumetric flask and further diluted to the mark. The solution was then transferred into a quartz cuvette cell (path length 1.0 cm) and the absorbance was measured at 230 nm ($\varepsilon = 63$ L cm$^{-1}$ cm$^{-1}$)$^{222}$. This was measured using double beam Perkin Elmer Lambda 35 UV-visible spectrometer. This standardization was conducted once a week provided that the solution was stored away from light and was covered with Al foil to avoid photo degradation.

3.4.2.14 Preparation of carbonate buffer (Na$_2$CO$_3$/NaHCO$_3$)

A standard procedure was followed (as below) for the preparation of 0.01 mol L$^{-1}$ NaHCO$_3$/NaHCO$_3$ (carbonate) buffer solutions pH 9.5.$^{223}$ The pH of each solution was measured with a Sartorius PB-10 pH meter fitted with a Sartorius pH/ATC electrode. The pH meter was calibrated prior to use with standard TPS buffer solutions at pH 4.00 and 9.18. Each pH measurement was conducted at the same temperature as required for the diode array analysis.

3.4.2.15 Preparation of 0.1 mol L$^{-1}$ Na$_2$CO$_3$

Anhydrous Na$_2$CO$_3$ (ca. 10. 599 g)$^2$ was weighed into a clean 50 mL beaker and then transferred the solid anhydrous Na$_2$CO$_3$ into a clean 1.00 L volumetric flask before adding deionized water (ca. 500 mL). The solid was dissolved and the solution made up to the mark with deionized water.

3.4.2.16 Preparation of 0.1 mol L$^{-1}$ NaHCO$_3$

NaHCO$_3$ (ca. 8.4 g)$^2$ was weighed into a clean 50 mL beaker and then transferred to a clean 1.00 L volumetric flask before adding deionized water (ca. 500 mL). The solid was dissolved and the solution made up to the mark with deionized water.

3.4.2.17 Purification of Orange (II) dye sodium ([4-{2-hydroxynaphthalyl]-benzenesulfon

Orange (II) dye stock solution (impure) was prepared in a solution of methanol and deionized water (9:1 ratio), (4.5 mL methanol, 0.5 mL deionized water). This was achieved by slowly
adding solid orange (II) dye (200 mg) to this solution with stirring. Any insoluble material remaining was removed by filtration. A medium pressure reverse phase chromatography column (C18, 25 x 0.46 cm, 10 µm) was prepared and conditioned with H2O/methanol (90%/10%) eluent. The orange (II) solution was injected onto the column and eluted with H2O/methanol (90%/10%). The intense orange band was collected in a 500 mL beaker. The solution volume was reduced using a rotatory evaporator until crystals were produced. The remaining solution was then removed using a vacuum pump to give pure crystals of orange (II) (126.3 mg).

3.4.2.18 Diode Array UV-visible spectrometer
For the absorbance measurements, a diode array UV-VIS spectrometer was used. This consisted of an Ocean Optics LS-1 tungsten halogen lamp, connected with fibre optic cables to a cuvette holder, which was in turn connected to a USB2000-VIS-NIR detector operating between 350 and 1000 nm. The temperature was controlled within ± 0.01 °C via a Quantum Northwest TC 125 temperature control unit. The stirring rate of the magnetic stirring bar in the cuvette could be controlled on this unit. A water pump (Little Giant Pump Company, Oklahoma City, U.S.A) was used as part of the temperature control system of the cuvette holder. OOLbase32 software version 2.0.6.2 (Ocean Optics) was used to obtain the data at a single wavelength. Each spectrum was acquired at the maximum rate of one reading every 0.5 seconds.

3.4.2.19 Method used to prepare a standard calibration curve of rate of hydrogen peroxide bleaching of standard orange (II) solution vs concentration of (Na)2[FeIII(Cl)B* (FeB*)]
An aliquot of Orange (II) solution (0.500 mL, 1 mmol L⁻¹) was added to a 10 mL volumetric flask. The solution was made up to the mark with carbonate buffer (0.01 mol L⁻¹, pH 9.5), giving an Orange (II) dye concentration of (50 µmol L⁻¹). An aliquot of this solution (3.00 mL) was then transferred to a quartz cuvette (path length 1.0 cm) with a 5 mm Teflon stirrer bar. The cuvette was placed in the temperature controlled holder at 25°C, and this was left for 5 min to equilibrate. An aliquot of (Na)2[FeIII(Cl)B* solution (60 µL, 5 x 10⁻⁵ mol L⁻¹) was added to the cuvette to give a final concentration of (1.00 µmol L⁻¹). An aliquot of H2O2 (12.31 µL, 0.2 mol L⁻¹) was then added to the cuvette to give a final H2O2 concentration of (1.00 mmol L⁻¹). The absorbance of the solution was then immediately measured for every 0.5 second at 483 nm. This procedure was repeated for solutions with different concentrations of
(Na)$_2$[Fe$^{III}$(Cl)B$^*$ (0.1, 0.2, 0.5, 1, 2, 5 µmol L$^{-1}$). For each experiment, triplicate runs were carried out$^{219}$.

In these experiments the absorbance starts to decrease with time as the Orange (II) dye is bleached. The experiment was stopped once the absorbance stopped dropping and plateaued. The initial rate of oxidation was determined by measure the slope of the plot of absorbance against time when oxidation of the dye did not exceed 10-20%. This slope was then divided by the extinction coefficient for orange (II) dye, (23,000 L mol$^{-1}$ cm$^{-1}$)$^3$ to give the initial rate in units of (mol L$^{-1}$ s$^{-1}$). The data was plotted using Sigma Plot for Windows, version 10. Each point recorded was the average of triplicate measurements.

For the standard calibration curve for the initial rate of reaction vs hydrogen peroxide concentration, the same procedure was followed but the conditions slightly changed. The [FeB$^*$] was set to 2 µmol L$^{-1}$ while the concentrations of the Orange (II) dye and carbonate buffer remained the same (50 µmol L$^{-1}$ and 0.01 mol L$^{-1}$) respectively. The [peroxide concentrations prepared and used were 0.10, 0.30, 0.50, 0.70, and 1.0) mmol L$^{-1}$.

For standard calibration curve of FeB$^J$ (C$_{16}$H$_{16}$ClFeK$_2$N$_4$O$_4$)), the same procedure used for FeB$^*$ was followed but the conditions were changed slightly. [H$_2$O$_2$] was set to 1.0 mM while the concentration of Orange (II) dye and carbonate buffer remained the same (50 µmol L$^{-1}$, 0.01 mol L$^{-1}$ at pH 9.5 and 11.0) respectively. The FeB$^J$ concentrations used were 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 mmol L$^{-1}$.

3.4.2.20 Preparation of orange (II) dye stock solution in carbonate buffer pH 9.5, temp 25 °C
Orange (II) dye stock solution (1.0014 mmol L$^{-1}$) was prepared by weighing 17.54 mg pure orange (II) solid into (50 mL) clean and dry volumetric flasks before dissolving and making up to the mark with deionised water. The solution was then wrapped in Al foil and stored in the dark. The solution could last for a few months without degradation. Orange (II) $\lambda$ max 483 nm$^{224}$

3.4.2.21 Method to investigate the permeation of carbonate buffer (0.01 M) through backing 2431 ND, 2471 and polyester backing.
Prepared 500 mL carbonate buffer (0.01 M, pH 9.5, temp 25 °C) $^2$. The novatexx backing was preconditioned in water at least one day prior to using in experiments. The U-tube glass joint was clamped together with a sample of the backing held between the two halves. Para-film was
added to the gasket prior to assembly to ensure no leaks occurred. The solutions were stirred at ca. 500 rpm and the openings of the tubes were covered with watch glasses.

3.4.2.22 Method for obtaining calibration curve in homogenous system

The selected buffer solution was made up as discussed in section 3.4.2.14 to the required pH. Solutions of (Et4N)2[FeIII(Cl)B*] (178.5 µL, 56.01 µmol L⁻¹) and orange II dye (0.245 mL, 1.837 mmol L⁻¹) were added to a 10 mL volumetric flask and made up to the mark with the required buffer, giving a (Et4N)2[FeIII(Cl)B*] concentration of 1.0 µmol L⁻¹ and orange II dye of 45 µmol L⁻¹. An aliquot of this solution (3.0 mL) was added to a quartz cuvette (pathlength 1.0 cm) with a 5 mm Teflon stirrer bar. The cuvette was then placed in a temperature controlled holder at 25 °C, and this was left for five minutes to equilibrate. An aliquot of hydrogen peroxide solution (14 µL, 0.214 mol L⁻¹) was added to the cuvette cell giving a H₂O₂ concentration of 1.0 mmol L⁻¹, and the absorbance at 483 nm was recorded every 0.5 seconds with an Ocean Optics UV-vis instrument comprising an LS-1 tungsten halogen lamp and a USB2000-VIS-NIR detector operating between 350 and 1000 nm. The temperature was controlled within ± 0.01 °C via a Quantum Northwest TC125 temperature control unit. For each experiment triplicate measurements were made and the absorbance results were found to be within ± 0.05. Initial rates of orange II oxidation were calculated from the slope of absorbance versus time plots (when the oxidation of the dye did not exceed 10–20%) and using the extinction coefficient for orange II at each pH. The first ten data points (5 seconds) were excluded in each case to allow time for sufficient mixing of the hydrogen peroxide. The initial rate reported is the mean of three samples at each pH. The same procedure was followed in obtaining the results for (NEt₄)[FeII(H₂O)B₃].

3.4.2.23 Typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored FeB* with (1:1) mole ratio

In a typical experiment: solution volume was 20 mL, buffer was carbonate/bicarbonate (0.01 M, pH 9.5), [H₂O₂] was 1.0 mM (0.11 mL, 0.18 M), [Orange II] was 50 µM (1.0 µmole), catalyst was FeB* (1.0 µmole anchored on a circular SCF 35 mm in diameter) prepared a day prior to the experiment. (The SCF used was preconditioned by standing in buffer solution (carbonate/bicarbonate (0.01 M, pH 9.5) for 24 hours before any catalyst was added to the SCF). The prepared SF PCMS +NMP membrane was immersed in 50 µM FeB* ((Mᵣ of FeB* used was 667.32, this was the corrected molar mass given by GreenOx for the sample which accounts for the impurities present), 20 mL solution made up in carbonate buffer solution (0.01 M, pH 9.5) with stirring at 100 rpm overnight. The SCF was then washed with deionized
water and immersed in fresh buffer with stirring (100 rpm) few times to ensure no leaching occurs. The SCF was prepared from five 50 µm coatings of a PVBC polymer cross-linked with 1, 6-diaminohexane on a polypropylene backing. The mole ratios for H₂O₂: Orange II: FeB for this typical example is 1: 1: 20. The stirring speed was 750 rpm and the time of the reaction was between 10 to 30 minutes. After a set series of time, an aliquot of this solution (3.0 mL) was added to a quartz cuvette (pathlength 1.0 cm) with a 5 mm Teflon stirrer bar. The cuvette was then placed in a temperature controlled holder at 25 °C, and this and the absorbance was monitored quickly at 483 nm was recorded every 0.5 seconds with an Ocean Optics UV-vis instrument comprising an LS-1 tungsten halogen lamp and a USB2000-VIS-NIR detector operating between 350 and 1000 nm. The temperature was controlled within ± 0.01 °C via a Quantum Northwest TC125 temperature control unit. For certain experiment triplicate measurements were made and the absorbance results were found to be within ± 0.05. The same aliquot was returned back to beaker while the solution was continued stirring and the absorbance was constantly measured until the solution turn colourless.

3.4.2.24 typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored ammonium molybdate tetrahydrate with (1:1) mole ratio

The same procedure was used as in section 3.4.2.22 except the catalyst used here is ammonium molybdate tetrahydrate. Prior to the experiment, the prepared SF PCMS +NMP membrane was immersed in 50 µM ammonium molybdate tetrahydrate (Mr 1235.86), 20 mL solution made up in deionised water with stirring at 100 rpm overnight. The SCF was then washed with deionized water and immersed in fresh buffer with stirring (100 rpm) few times (30 minute each) to ensure no leaching occurs.

3.4.2.25 typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored sodium tungstate dihydrate with (1:1) mole ratio

The same procedure was used as in section 3.4.2.22 except the catalyst used here is sodium tungstate dihydrate. Prior to the experiment, the prepared SF PCMS +NMP membrane was immersed in 50 µM sodium tungstate dihydrate (Mr 329.85), 20 mL solution made up in deionised water with stirring at 100 rpm overnight. The SCF was then washed with deionized water and immersed in fresh buffer with stirring (100 rpm) few times (30 minute each) to ensure no leaching occurs.
3.4.2.26 Typical bleaching experiment in beaker using orange II dye with a PCMS+NMP polymer and anchored FeB\(^J\) \((C_{16}H_{16}ClFeK_2NiO_4)\) with (1:1) mole ratio

The same procedure was used as in section 3.4.2.22 except the catalyst used here is FeB\(^J\). Prior to the experiment, the prepared SF PCMS +NMP membrane was immersed in 50 \(\mu\)M FeB\(^J\) (Mr 497.817), 20 mL solution made up in carbonate buffer solution (0.01 M, pH 9.5) with stirring at 100 rpm overnight. The SCF was then washed with deionized water and immersed in fresh buffer with stirring (100 rpm) few times (30 minute each) to ensure no leaching occurs.

3.4.2.27 Preparation of pinacyanol chloride stock solution

A stock solution of PCl was prepared by adding PCl (0.389 mg, Mr 388.93) to a 50.00 mL volumetric flask, dissolving the solid in 40 mL of carbonate buffer solution (0.01 M, pH 9.5) and then making the solution up to the mark with more buffer solution. This volumetric flask was covered with Al Foil to avoid photo-degradation. For reactions involving the bleaching of PCl, 1.00 mL of this stock solution was added to the reaction mixture (19.0 mL) to give a total reaction volume of 20.0 mL with the concentration of PCl being 50 \(\mu\)M. PCl \(\lambda_{max}\) 600 nm\(^{225}\).

3.4.2.28 Preparation of safranine O stock solution

A stock solution of safranine O was prepared by adding safranine O (0.35 mg, Mr 350.85) to a 50.00 mL volumetric flask, dissolving the solid in 40 mL of carbonate buffer solution (0.01 M, pH 9.5) and then making the solution up to the mark with more buffer solution. This volumetric flask was covered with Al Foil to avoid photo-degradation. For reactions involving the bleaching of safranine O, 1.00 mL of this stock solution was added to the reaction mixture (19.0 mL) to give a total reaction volume of 20.0 mL with the concentration of safranine O being 50 \(\mu\)M. Safranine O \(\lambda_{max}\) 518 nm\(^{226}\).

3.4.2.29 Preparation of phenolphthalein stock solution

A stock solution of phenolphthalein was prepared by adding phenolphthalein (0.32 mg, Mr 318.32) to a 50.00 mL volumetric flask, dissolving the solid in 40 mL of carbonate buffer solution (0.01 M, pH 9.5) and then making the solution up to the mark with more buffer solution. This volumetric flask was covered with Al Foil to avoid photo-degradation. For reactions involving the bleaching of phenolphthalein, 1.00 mL of this stock solution was added to the reaction mixture (19.0 mL) to give a total reaction volume of 20.0 mL with the concentration of phenolphthalein being 50 \(\mu\)M. Phenolphthalein \(\lambda_{max}\) 550 nm\(^{227}\).
3.4.2.30 Typical bleaching experiments in the U-tube system using orange II dye with a PCMS+NMP polymer and anchored FeB* with (1:1) mole ratio

A day prior to the experiment, the prepared SF PCMS +NMP membrane was placed on a wire loop and immersed in FeB* solution (50 µM, 30 mL, made up in buffer solution, 0.01 M, pH 9.5) (M_t of FeB* used was 667.32, this was the corrected molar mass given by GreenOx for this sample which accounts for the impurities present) and the solution stirred at 100 rpm overnight. The SCF was then removed, washed with deionized water and immersed (on the wire loop) in fresh buffer solution (20 mL) with stirring (100 rpm) few times to ensure no leaching occurs. In a typical experiment the circular (35 mm diameter) SCF was fixed between the arms of the 3 cm diameter U-tube. The SCF was prepared from five nominally 50 µm coatings of a PCMS polymer cross-linked with 1,6-diaminohexane on a polypropylene backing and contained FeB* (1.5 µmole). The two arms of the U-tube were filled with DI water, (30 mL and 100 mL respectively) and the apparatus left to stand for 30 minutes to ensure the SCF allowed water to slowly permeate (steady flux) and that there were no leaks. The water was removed and replaced in one arm by the substrate solution (30 mL) which contained Orange II (50 µM, 1.5 µmole) in deionized water (pH 7.0). The oxidant solution containing H_2O_2 (100 mL, 1.0 mM, which was prepared by addition of stock H_2O_2 solution (0.56 mL, 0.18 M) to carbonate/bicarbonate buffer 0.01 M, pH 11.0, and making the volume up to 100 mL with buffer solution) was placed in the other arm of the U-tube apparatus. Both solutions were stirred at 750 rpm for 30 minutes. At set times during this period an aliquot (3.0 mL) of the orange II solution was removed, the absorbance measured and then returned to the U-tube apparatus.

3.4.2.31 typical bleaching experiment in small cross flow system using orange II dye with a PCMS+NMP polymer and anchored FeB* with (1:1) mole ratio

In a typical experiment the SCF was clamped between the two halves of the cross-flow apparatus. The SCF was prepared from five nominally 50 µm coatings of a PCMS polymer cross-linked with 1,6-diaminohexane on a polypropylene backing and contained FeB* (1.0 µmole). The hydrogen peroxide oxidant solution (1.0 mM) in carbonate/bicarbonate buffer (0.01 M, pH 11.0) filled the bottom chamber of the cross-flow apparatus and was connected by tubes to a reservoir that could be adjusted in height. An open acrylic support was placed in this chamber to support the SCF. The hydrogen peroxide reservoir was raised 20 cm above the SCF in the cross-flow apparatus. The resulting small hydrostatic head produced a pressure differential across the SCF that caused the perfusion of the hydrogen peroxide through the film. The solution containing the orange (II) substrate (50 µM) in deionized water (pH 7.0) was then
pumped by a peristaltic pump at a rate of 5.0 mL/minute through the other chamber of the cross-flow apparatus. A plastic mesh in this chamber sat on top of the SCF to induce turbulence to the flow of the orange (II) solution. The dimensions of the SCF exposed to the flowing orange II solution was 4 cm x 9 cm x 0.3 cm. Under these conditions the absorbance of the orange II solution entering the cross-flow apparatus (initial absorbance) was 1.05 and the absorbance of the solution exiting the apparatus was 0.15. This indicates that approximately 85% of the dye was oxidised during this one pass through the apparatus. Therefore, under these conditions, the 36 cm² SCF can treat 5 mL of solution per minute.
4.1 Summary to chapter 4

This chapter starts by introducing endocrine disrupting compounds (EDCs), how their mode of action takes place and the effect of EDCs on humans and animals. Then 3 EDCs, EE₂, TCS and BPA are introduced and discussed in detail. In addition this chapter then shows how oxidative destruction of these EDCs takes place using the FeB*/H₂O₂ heterogeneous oxidation systems discussed in Chapter 3 and comparisons are made with oxidations carried out by the FeB*/H₂O₂ homogenous system.

4.2 Introduction 17α- Ethynylestradiol

The synthetic estrogen known as EE₂ (17α-ethynylestradiol) is an active ingredient commonly used in oral contraceptive pills. EE₂ is a type of endocrine disruptor compound which is defined by Environmental Protection Agency (EPA) as xenobiotics (i.e. agents foreign to an organism) that interfere with the “synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behaviour”²²⁸. EE₂ is one of the common compounds found in municipal agricultural and industrial wastewater where human excretion is the main source of xenoestrogens in an aquatic environment²²⁹. Various researchers have focused on the effects of EE₂ since abnormal sexual development in animals and decreases in the average numbers of human spermatozoa have been widely reported²³⁰. In addition, EE₂ also interferes with the normal functioning of endocrine systems, thus affecting reproduction and development in wildlife. One of the significant impacts of long term exposure to EE₂ is the feminisation of female fish due to the formation of plasma vitellogenin. The structure of EE₂ is shown in Figure 226²³¹:

![Figure 226: 17α-Ethynylestradiol](image-url)
EE₂ is susceptible to photo-degradation but more resistant towards biodegradable reaction. As a result, standard treatments like coagulation and activated sludge processes are not effective in treating EE₂ while more complex treatments such as granular activated carbon, membranes and advances oxidation processes have shown satisfactory results. Despite more efficient treatment, these approach still have drawbacks including the release of many by-products that could have higher estrogenic activity than their precursors. Selected physicochemical properties and estrogenic (androgenic) activity of EE₂ are shown in Table 93.

<table>
<thead>
<tr>
<th>Name of EDC</th>
<th>Molar mass (g/mol)</th>
<th>Water solubility (mg/L)</th>
<th>Log Kow</th>
<th>Estrogenic potency (YES)</th>
<th>Estrogenic potency (E-screen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EE₂</td>
<td>296.4</td>
<td>116</td>
<td>2.45</td>
<td>1.19,1.5</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 93: Physicochemical properties and estrogenic activity of EE₂

### 4.3 Introduction to Bisphenol A

In early 1940, manufacturing companies started to use Bisphenol A (BPA) (also known as 2,2-bis(4-hydroxylphenyl)propane) mainly for production of plastics. BPA is an organic compound where 2 phenol groups are connected together by a methyl bridge with 2 methyl substituents as depicted in Figure 227 below:

![Figure 227: Bisphenol A](image)

BPA is a molecule that binds with other molecules to form polymers, such as polycarbonate. BPA is commonly used for production of phenol resins, polyacrylates, and polyesters but mainly for the production of epoxy resins and polycarbonate plastics. Hence, increased exposure to BPA through the use of consumer products that include drinking bottles, dental seals, microwaved food products, toys and medical devices can lead to disruptive effects on the endocrine system of humans.
There are various ways BPA can end up in the aquatic environment but the primary route of BPA contamination is effluents from wastewater treatment plants and landfill sites\textsuperscript{237}. BPA can also contaminate water by migration of BPA from BPA based products.

BPA is a known endocrine disruptor and is acutely toxic to aquatic organisms in the range 1000-10,000 \(\mu\text{g/L}\) for fresh water and marine species\textsuperscript{238}. Not only is it toxic on its own, but it can also form chlorinated derivatives on contact with sodium hypochlorite. Sodium hypochlorite, is a widely known chemical used as a bleaching agent in pulp and paper factories and in households, and as a disinfectant in wastewater treatment\textsuperscript{239}. Examples of chlorinated derivatives of BPA are shown in Figure 228:

\textbf{Figure 228: Chlorinated derivatives of BPA}
Overall these derivatives showed more potent estrogenic activity (3-38 times that BPA alone) in an agonist assay using a two-hybrid yeast system.

In addition, BPA can also be found in sediments where it originated from tetrabromobisphenol A (TBBPA) which is most widely used as a flame retardant in the production of many plastic polymers and electronic circuit boards\textsuperscript{236}. This conversion mainly occurs under anaerobic conditions within approximately 3 months. Moreover, conversion of TBBPA to BPA normally leads to the formation of intermediates such as mono-BBPA and di-BBPA which also show estrogenic activities. The structure of TBBPA and other intermediates are shown in Figure 229:

![Chemical structure of TBBPA, tri-BBPA, di-BBPA and mono-BPA](image)

Figure 229: Chemical structure of TBBPA, tri-BBPA, di-BBPA and mono-BPA
4.3.1 Endocrine-disruptive effects of BPA on Aquatic Organisms

Fish and frogs are vertebrates and snails are invertebrates that are normally chosen to investigate the endocrine-disruptive effects of BPA. The main endocrine-disruptive effects of BPA on fish are vitellogenin induction, abnormality of reproductive systems and the induction of embryonic deformities. In addition, induction of feminization, malformation of organs, and high mortality are possible endocrine-disruptive effects of BPA exposure to frogs. In freshwater snails, the main endocrine-disruptive effects of BPA are abnormality of reproductive systems and induction of imposex.

4.4 Introduction to Triclosan

Triclosan is a synthetic, lipid-soluble, broad spectrum anti-microbial agent introduced in 1972\(^{240}\). In the United States, triclosan has been used for more than 40 years in personal care products, household items, medical devices and hospitals to control the spread of bacteria. The structure of TCS is shown in Figure 230\(^{240}\).

![Figure 230: Triclosan](image)

Due to its popularity, annual production of TCS has increased during the past 20 years to values of more than 10 million pounds per year\(^{241}\). As a consequence, TCS can be found in finished drinking water, surface water, wastewater, and environmental sediments, as well as in the bile of wild fish, indicating extensive contamination of aquatic ecosystems (7-10). In addition, TCS can also be found in human breast milk as well as in urine.

This is potentially a major problem for the human population since TCS is a compound that also known to possess endocrine disruptor effects. Studies showed that TCS was weakly androgenic, causing changes in the fin length and sex ratio of Japanese Medaka fish while
another study showed that triclosan was toxic and weakly estrogenic with the potential to induce vitellogenin in male Medaka. In addition, study with North American bullfrogs shows that exposure to TCS during the premetamorphic stage altered the rate of triiodothyronine-induced metamorphosis and thyroid hormone receptor mRNA expression. Typical routes that are now being used to eliminate TCS such as treatment with sodium hypochlorite, and photo degradation suffer several drawbacks such as formation of chlorinated derivatives and/or other potential toxic intermediate products. As a consequence, other more environmental friendly and benign treatments have been extensively studied to overcome this problem.

4.5 Mode of Action of Endocrine Disruptors
Currently, most of the Endocrine Disruptor Chemicals (EDC) have been discovered to cause problems by imitating endogenous hormones. These chemicals can function as agonists or antagonists of hormone receptors to either block or generate hormone-mediated responses. They can also act through other alternative pathways such as by inhibiting or stimulating enzymes associated with hormones synthesis, metabolism or excretion. Less well-characterized pathways of action include reacting directly or indirectly with endogenous hormones or altering hormone receptor numbers or affinities. EDCs with anti-estrogenic properties have existed for past 50 years and have been found to have the effect of blocking the activation of the estrogen receptor or by binding the aryl hydrocarbon (Ah) receptor, hence leading to induction of Ah-responsive genes that can have a spectrum of antiestrogenic effects. Anti-estrogens can create an androgenic environment, producing symptoms similar to those of androgenic exposure. Examples of compounds with antiandrogenic activities are pharmaceuticals such as tamoxifen, fulvestrant, raloxifene and some of the polyaromatic hydrocarbon (PAH) such as anthracene.

Chemicals with antiandrogenic activity can also have similar overall effect to estrogens. Examples of these chemicals can be flutamide (anticancer agents), 17α-methyltestosterone (for testosterone deficiently) and pesticides (e.g. p,p'-DDE, a metabolite of DDT, the herbicides linuron and diuron, and metabolites of the fungicide vinclozolin). These chemicals can cause the feminizing effects observed in wildlife populations caused by these chemicals blocking the androgen receptors rather than as a consequence of exposure to environmental estrogens. In addition, significant evidence also shows there are links between increases in the group of
disorders referred to as testicular dysgenesis syndrome (TDS) in humans, which originate
during fetal life, and exposure to environmental chemicals with antiandrogenic activity\textsuperscript{249}.

There is also another class of chemicals that have the ability to disrupt thyroid function. These
structures are believed to have a high degree of structural similarity to thyroid hormones and
act via binding interference with endogenous thyroid hormone receptors. Thyroid hormones
are responsible for normal development and function of the brain and sex organs, as well as
metamorphosis in amphibians, and in growth and regulation of metabolic processes\textsuperscript{250}. Hence
interference of normal functioning can disrupt a very wide range of biological processes\textsuperscript{244}.

Other modes of hormonal disruption have been identified, but there are considerably less data
for these. These modes include those acting via the progesterone or Ah receptors, corticosteroid
axis, and the enzyme systems involved with steroid biosynthesis. Chemicals interacting with
the progesterone receptors can impact both reproductive and behavioural responses, notably in
fish, in which progesterones can function as pheromones.\textsuperscript{251} Examples of these progesterones
are contraceptive pharmaceuticals such as levonorgestrel, desogestrel, gestodene and
norethisterone.

\subsection*{4.5.1 Altered hormone synthesis}

Some chemicals such as aminoglutethimide, cyanoketone and ketoconazole believe to hinder
specific enzymatic steps in the biosynthetic pathway of steroidogenesis. In addition some
fungicides block estrogen biosynthesis by inhibiting aromatase activity. Environmental
estrogens and antiandrogens alter protein hormone synthesis induced by gonadal steroids\textsuperscript{252}. Both estrogen and testosterone have been shown to affect the pituitary hormone synthesis
directly or through changes in the glycosylation of LH and FSH\textsuperscript{253}. A decrease in glycosylation
of these glycoproteins reduces the biological activity of the hormones. Any environmental
compound that mimics or antagonizes the action of these hormones could presumably alter
glycosylation.

\subsection*{4.5.2 Altered hormone storage or release}

Steroid hormones do not appear to be stored intracellularly within membranous secretory
granules. For instance, testosterone is synthesized by Leydig cells of the testis and released on
activation of the LH receptor\textsuperscript{252}. Thus, compounds that block the LH receptor or the activation
of the 3'5'-cyclic AMP-dependent cascade, involved in testosterone biosynthesis can rapidly
alter the secretion of this hormone. The release of many protein hormones is dependent on the
activation of secondary messenger pathways, such as cAMP, phosphatidylinositol, inositol 1,-
4,5-triphosphate (IP₃), tyrosine kinase and Ca⁺. Interference with these processes consequently will alter the serum levels (availability) of many hormones. Several metal cations have been shown to disrupt pituitary hormone release, presumably by interfering with Ca²⁺ flux²⁵⁴.

4.5.3 Altered hormone transport and clearance
Hormones are generally transported in blood either in the free or bound state. Steroid hormones are transported in the blood by specialized transport (carrier) proteins known as sex-steroid hormone-binding globulin (SHBG) or testosterone-estrogen-binding globulin (TEBG). Controlling the concentration of these binding globulins in the blood is of practical significance because increases or decreases of the amount of these could affect steroid hormone availability. For instance DDT analogs are potent inducers of hepatic microsomal monoxygenase activities in vivo²⁵⁵. Induction of this monoxygenase activity by treatment with DDT analogs could possibly cause a decrease in testicular androgen as a result of enhanced degradation. Similarly treatment with lindane (gamma-hexachlorohexane) has been reported to increase the clearance of estrogen²⁵⁶.

4.5.4 Altered hormone receptor recognition/binding
Hormones elicit responses on their respective target tissues through direct interactions with either intracellular receptors or membrane-bound receptors. Specific binding of the natural ligand to its receptor is a critical step in hormone function. Intracellular (nuclear) receptors, such as those for sex steroids, adrenal steroids. Thyroid hormones, vitamin D, and retinoic acid, regulate gene transcription in a ligand-dependent manner through their interaction with specific DNA sequences (response elements). Several types of environmental agents may alter this process by mimicking the natural ligand and acting as an agonist or by inhibiting binding and acting as an antagonist. Compounds that can do this include chlordecone, DDT, PCB, methoxychlor and alkylphenols. The anti-androgenic action of the dicarboximide fungicide vinclozolin is the result of an affinity of the metabolite of this compound for the androgen receptor²⁵⁷. Fascinatingly the DDT metabolite also has been found to bind to androgen receptors and block testosterone induced cellular responses in vitro²⁵⁷.

Many of the chemicals classified as environmental estrogens can actually inhibit binding to more than one type of intracellular receptor. For example, o,p-DDT and chlordecone can inhibit endogenous ligand binding to the estrogen and progesterone receptors, with each compound having IC₅₀ values that are nearly identical for the two receptors. Receptors for protein hormones are located on and in the cell membrane. When these hormones bind to their
receptors, transduction of a signal across the membrane is mediated by the activation of secondary messenger systems. These may include (a) alterations in G-protein/cAMP-dependent protein kinase A (e.g., after LH stimulation of the Leydig cell), (b) phosphatidylinositol regulation of protein kinase C and inositol triphosphate (e.g., after GnRH stimulation of gonadotrophs; thyrotropin releasing hormone stimulation of thyrotrhops), (c) tyrosine kinase (e.g., after insulin binding to the membrane receptor), and (d) calcium ion flux. Xenobiotics thus can disrupt signal transduction of peptide hormones if they interfere with one or more of these processes.

4.5.5 Altered Hormone Post-Receptor Activation

Once the endogenous ligand or an agonist binds to its receptor, a cascade of events are initiated, indicative of the appropriate cellular response. This includes the response necessary for signal transduction across the membrane, or in the case of nuclear receptors, the initiation of transcription and protein synthesis. A variety of environmental compounds can interfere with the membrane’s secondary messenger systems. For example, cellular responses that are dependent on the flux of calcium ions through the membrane (and the initiation of the calcium/Calmodulin-dependent cellular response) are altered by a variety of environmental toxicants. Interestingly, the well-known antiestrogen tamoxifen also inhibits protein kinase C activity\textsuperscript{258}. Alternatively, the phorbol esters are known to mimic diacylglycerol and enhance protein kinase C activity. Steroid hormone receptor activation can be modified by indirect mechanisms, such as a down-regulation of the receptor (temporary decreased sensitivity to ligand) as seen after TCDD exposure (including the estrogen, progesterone, and glucocorticoid receptors)\textsuperscript{259,260}. Consequently, because of the diverse known pathways of endocrine disruption, any assessment must consider the net result of all influences on hormone receptor function and feedback regulation.

4.6 EE\textsubscript{2} oxidation with the FeB*/H\textsubscript{2}O\textsubscript{2} homogenous system

For the past decades, extensive research has been investigated to destroy EDCs using various conditions in homogenous systems. The environmentally benign homogenous system of interest involving the Fe-TAML/H\textsubscript{2}O\textsubscript{2} catalytic oxidation system is a promising method to eliminate estrogenticity from wastewater contaminated by natural and synthetic estrogens, which are environmental persistent and resistant to bacterial degradation\textsuperscript{240}. Studies have
shown that Fe-TAML/H₂O₂ in homogenous systems were able to destroy 17α-ethynylestradiol (EE₂) which is the active component of oral contraceptive pills. This was investigated using EE₂ (80 µM with the Fe-TAML, FeB* (83 nM), in conjunction with H₂O₂ (4 mM) as an oxidant for 60 min at pH 10 in buffer solution. Under these conditions, > 95% oxidative removal of EE₂ with accompanying loss of estrogenicity (ca. 95% reduction) was observed. In addition, the studies also discovered that partial oxidation of EE₂ by Fe-TAML (FeB*)/H₂O₂ formed intermediates which were the epimers 17α-ethynyl-1,4-estradiene-10α,17β-diol-3-one and 17α-ethynyl-1,4-estradiene-10β,17β-diol-3-one. Significantly, this product mixture exhibited slightly higher estrogenicity values than EE₂ itself as confirmed by YES bioassay. Nevertheless, upon further treatment with FeB*/H₂O₂ the concentration of both intermediates slowly drops to zero within 60 min to form unidentified products which showed no estrogenicity. Prior to the reports of using Fe-TAML/H₂O₂ as an alternative system to destroy persistent contaminants, studies were conducted using embryonic zebrafish model to investigate the effects of long-term exposure to Fe-TAML. It was discovered that at concentrations of Fe-TAML ≤ 2 µM there was no toxicity effect on zebrafish that have had their protective chorions removed to increase bioavailability to test chemicals and thus making them more sensitive than zebrafish in the wild. Despite the effectiveness of this homogeneous catalytic oxidation system, there are several major disadvantages that limit its practical use in the environment. Firstly, the water being treated would have to be dosed with both catalyst and hydrogen peroxide, and if the commercially available catalyst FeB* is used the water would have to be made basic. The catalyst has a relatively short life-time and so degrades quickly and the amounts required to treat large volumes of water would make the treatment system very expensive. Nevertheless, it is a very good oxidation catalyst and if it could be made part of a heterogeneous catalytic system its use could become very favourable.
4.7 Oxidation of TCS and Bisphenol A with Fe-TAML/H₂O₂ in homogenous systems

Studies have been carried out recently using the Fe-TAML/H₂O₂ homogeneous system to destroy aqueous solutions of TCS and BPA. The Fe-TAML/H₂O₂ catalytic oxidation system mimics the activity of peroxidase enzymes. These catalyst systems have proven to be successfully used to efficiently remove endocrine disrupting chlorinated phenols in aqueous solution with concomitant reduction in estrogenicity of the solution. It has been shown that oxidative treatment using 4 nM FeB* and 4 mM H₂O₂ can successfully remove 43.8 µM BPA and 32.5 µM TCS within 60 minutes at pH 9.5 and 9.0, respectively. The rate of the oxidation reaction decreases rapidly as the pH drops below 9.0 in neutral or acidic condition (pH 6), effectively no oxidation takes place.

Estrogenicity of the products formed in these reactions was determined by the YES test. It is important to ensure that any by-product formed do not result in higher estrogenic activity than the parent compound. The results for BPA show that using (16, 24 and 40 nM FeB*) with 4 mM H₂O₂ gave significantly low residual estrogenic activity while using 4 nM FeB* showed 75% estrogenic activity was retained. The estrogenicity of the product mixture formed on oxidation of TCS could not be accurately determined because of the yeast lysing properties of residual TCS. The main product detected in the oxidative treatment of BPA and TCS using the conditions specified above were oxidatively coupled dimers, trimers and tetramers. These were detected by mass spectrometry.
In addition, the oxidation of BPA and triclosan was also dependent on the concentration of the FeB* catalyst. This study show that as the FeB* concentration increased from 4 nM to 40 nM, the time taken for complete bleaching reduced from roughly 3 hours to 30 minutes. In summary, even though this Fe-TAML/H2O2 homogenous system can successfully destroy BPA and TCS under this conditions with low estrogenicity by-product formed, application of this system to practical environmental remediation purposes is not feasible because of the limitations noted above. Hence in this study a more complex, heterogeneous system using the FeB*/H2O2 oxidation system was investigated with the aim of showing that it could be used to remove EDCs in large volumes of water in a practical way.

4.8 Calibration curves for HPCL analysis of BPA, EE2 and TCS

The ability of the SCFs to catalyse the oxidation of the real-world pollutants EE2, BPA and TCS using the simple beaker, U-tube and cross-flow apparatuses were studied. Due to time limitations the oxidation products formed in each case were not analysed. Instead, only the remaining amounts of pollutant after each reaction were determined. Clearly, in future work it will be very important to carefully study the oxidation products formed to ensure these products do not have the same toxicity problems as the pollutants themselves.

Before the catalytic oxidation reactions could be studied, the method of analysis of very small amounts of the pollutant compounds had to be selected and calibration curves obtained. Since HPLC had been reported as a very good method by which to carry out these261 this technique was used. The full details are given in the experimental section. A calibration curve was prepared for each of these compounds using the conditions detailed below. These calibration curves were used to determine the amount of un-oxidized compounds remaining after the oxidation reactions.
4.8.1 Calibration curve for BPA

A calibration curve for BPA was obtained using the HPLC UV detector set at 280 nm. This wavelength was chosen since it is wavelength at which the maximum absorption of BPA occurs\(^\text{264}\). The results are given in Table 94 and Figure 232.

![Calibration curve of BPA at 280 nm at retention time 10 min](image)

**Table 94: Condition for BPA calibration curve**

<table>
<thead>
<tr>
<th>Concentration (PPM)</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
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<td>9102</td>
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<td>0.75</td>
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<td>1</td>
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<td>3</td>
<td>99129</td>
</tr>
<tr>
<td>5</td>
<td>171773</td>
</tr>
</tbody>
</table>

**Figure 232: Calibration curve of BPA at 280 nm**
4.8.2 Calibration curve EE$_2$

Calibration curve of EE$_2$ was determined using the absorbance at 230 nm since $\lambda_{\text{max}}$ for EE$_2$ occurs at this wavelength. The results are given in Table 95 Figure 233.

![Calibration curve of EE$_2$ at 230 nm at retention time 14.8](image)

**Figure 233: Calibration curve of EE$_2$ at 230 nm**

<table>
<thead>
<tr>
<th>Concentration (PPM)</th>
<th>peak area</th>
</tr>
</thead>
<tbody>
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<tr>
<td>1</td>
<td>2405785</td>
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</tbody>
</table>

**Table 95: Condition for EE$_2$ calibration curve**
4.8.3 Calibration curve TCS

Calibration curve of TCS was determined using the absorbance at 230 nm since $\lambda_{\text{max}}$ for TCS occurs at this wavelength\textsuperscript{266}. The results are given in Table 96 and figure 234.

![Calibration curve of Triclosan at 280 nm at retention time 8 min](image)

Figure 234: Calibration curve of triclosan at 280 nm

<table>
<thead>
<tr>
<th>Concentration (PPM)</th>
<th>Peak area</th>
</tr>
</thead>
<tbody>
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<td>34718</td>
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<td>0.1</td>
<td>11555</td>
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</table>

Table 96: Condition for triclosan calibration curve
4.9 Reactions of BPA, EE₂ and TCS with SCFs in a beaker

Catalytic oxidation reactions of BPA, EE₂ and TCS using the SCFs were first carried out in a beaker using the same reaction procedures described in section 3.2. As before, the hydrogen peroxide and substrate were not separated by the SCF in this configuration.

4.9.1 Oxidation Reactions of Bisphenol A (BPA) using the SCFs in a beaker

A series of reactions of BPA were carried out using as catalyst a SCF (PCMS+ NMP) containing FeB*. For all reactions the concentration of BPA was 2 ppm (8.76 µM), the concentration of hydrogen peroxide was 1.0 mM and the stirring speed was 1000 rpm. The pH of the solutions was 7.0, 9.5 or 11.0, and carbonate buffer (0.01 M) solution was used to maintain the pH of the alkaline solutions. Different catalyst loadings (either 0.0175 µmole or 17.5 µmole, corresponding to catalyst:substrate mole ratios of 1:10 or 100:1) were used, and the reaction times were either 10 or 30 minutes.

The results obtained are collected in Table 97. Before the catalytic reactions were carried out a series of blank experiments were performed. These involved experiments in which a SF with no adsorbed FeB* was used (Blank 1), a SCF was present but no hydrogen peroxide was added (Blank 2) and no SCF was added (Blank 3). The results from these blank experiments are given in Table 97 where it can be seen that in each case 96-97% of the BPA present initially was recovered. Not only did this show that essentially no loss of BPA occurred through oxidation by hydrogen peroxide alone or adsorption onto the SCF, but that very nearly all the BPA could be recovered from solution by the solid phase extraction (SPE) method used.

The results of the catalytic oxidation reactions show that with a large amount of FeB* on the SCF at pH 9.5 all the EE₂ was oxidatively removed within 10 minutes (Entry 4). This showed that the SCF was indeed capable of very effectively removing BPA from solution through oxidation. At the same pH, but with much less catalyst on the SCF (catalyst:substrate) mole ratio 1:10) 9% of the BPA remained after 10 minutes of reaction (Entry 6). On changing the pH to 11.0, 5% remained (Entry 7) while at a pH of 7.0, 70% remained after 10 minutes (Entry 5). These results show that as expected the activity of the catalyst increases with increasing pH. However, the oxidative removal of 70% of the BPA in the reaction at pH 7.0 was very
significant as it strongly suggests that it might be possible to remove this pollutant using the SCFs at the neutral pH of most natural waters.

The oxidation of BPA under these conditions appeared to be very rapid and so the experiment with the small amount of catalyst at pH 9.5 was repeated, but the reaction was stopped after only 2 minutes. Even after this very short reaction time only 21% of the BPA remained (Entry 8). Oxidation of BPA using the SCF in this configuration was very fast indeed.

To explore whether the catalyst FeB\(^{\text{I}}\) could also catalyse the oxidation of BPA under these conditions, a reaction was carried out with a SCF containing a small amount of this catalyst (catalyst: substrate mole ratio 1:10) at pH 9.5 for 30 minutes (Entry 9). After this extended time 27% of the BPA was recovered. Although this iron TAML did catalyse the oxidation of BPA it was much less active than FeB\(^{\text{I}}\) under these conditions.
Oxidation reactions of BPA catalysed by SCFs using FeB*:

<table>
<thead>
<tr>
<th>Entry</th>
<th>[BPA] ppm</th>
<th>Mole ratio (FeB*: BPA)</th>
<th>pH</th>
<th>Reaction time (minute)</th>
<th>[H₂O₂] mM</th>
<th>(%) BPA remaining</th>
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<td>9.5</td>
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<td>97.0</td>
</tr>
<tr>
<td>Blank reaction 2</td>
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<td>(1:10)</td>
<td>9.5</td>
<td>30</td>
<td>-</td>
<td>96.0</td>
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<tr>
<td>Blank reaction 3 (No SCF)</td>
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<td>-</td>
<td>9.5</td>
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<td>96.0</td>
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</tbody>
</table>

Table 97: Summarized BPA oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB*

Oxidation reactions of BPA catalysed by SCFs using FeB↓:

<table>
<thead>
<tr>
<th>Entry</th>
<th>[BPA] ppm</th>
<th>Mole ratio (FeB*: BPA)</th>
<th>pH</th>
<th>Reaction time (minute)</th>
<th>[H₂O₂] mM</th>
<th>(%) BPA remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2.0</td>
<td>(1:10)</td>
<td>9.5</td>
<td>30</td>
<td>1.0</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Table 98: Summarized BPA oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB↓
4.9.2 Oxidation reactions of 17α-ethynylestradiol (EE₂) using the SCFs in a beaker

A series of catalytic oxidation reactions of 17α-ethynylestradiol (EE₂) was conducted in a beaker using different loadings of the catalyst FeB* or FeB⁺ (either 0.0135 µmole or 13.5 µmole, corresponding to catalyst: substrate mole ratios of 1:10 or 100:1) on SCFs, different pHs (7, 9.5, 11.0) and reaction times (5, 10, 30 minutes). In all cases the initial concentration of EE₂ was 2 ppm (6.75 µM), the concentration of hydrogen peroxide was 1.0 mM and the stirring speed was 1000 rpm. The SCFs were synthesised using a PCSM+NMP polymer. The conditions and results of the experiments are summarised in Table 99 and 100.

When very large amounts of catalyst were used on the SCF (13.5 µmole, catalyst:substrate mole ratios 100:1) complete oxidative removal of the EE₂ occurred in the reaction carried out for 30, 10 or even 5 minutes (Entries 10 – 12). If the pH was maintained at 9.5, and the amount of catalyst reduced to 0.0135 µmole (catalyst: substrate mole ratio 1:10), 11% of the initial EE₂ remained after 10 minutes (Entry 14). Reducing the pH to 7.0 with this same amount of catalyst on the SCF resulted in a much higher amount of EE₂ remaining (35%, Entry 13) after 10 minutes. On the other hand, if the solution was made more alkaline (pH 11.0), only 5% of the EE₂ remained after 10 minutes (Entry 15). Clearly the same trend of increasing rate with higher pH that was observed for the BPA oxidations also occurred for these reactions. For reactions at pH 11.0 with low levels of catalyst that were stopped after 5 or 2 minutes, the amount of EE₂ remaining was 9% and 14%, respectively (Entries 16 and 17). As expected, reducing the time of reaction resulted in more unreacted EE₂, but remarkably the majority of this compound was oxidatively removed (86%) after just 2 minutes of reaction.

Similar reactions were also investigated with the different catalyst FeB⁺ adsorbed onto the SCF (either 0.0135 µmole or 13.5 µmole), corresponding to catalyst: substrate mole ratios of 1:10 or 100:1). For the reaction at high catalyst level (13.5 µmole FeB⁺) on the SCF and the pH 9.5, only a very small amount of EE₂ (5%) remained unchanged after 30 minutes (Entry 22). As with the reactions with FeB* high levels of catalyst caused essentially complete oxidative removal of EE₂. For the reaction at pH 9.5 with a much smaller amount of catalyst (0.0135 µmole, catalyst:substrate mole ratio 1:10), only 9% of the EE₂ remained after 10 minutes (Entry 19). If the pH was increased to 11.0, the amount of oxidative removal remained the same and again 9% of the EE₂ remained after 10 minutes (Entry 20). When the pH was reduced to 7.0,
the oxidation was slowed very significantly and after 10 minutes 71% of the EE$_2$ remained unchanged (Entry 18). Clearly there was a large effect of pH on the amount of EE$_2$ oxidatively removed over 10 minutes. If the reaction at pH 9.5 was stopped after the shorter time of 5 minutes, a relatively large amount (32%) of the EE$_2$ remained unchanged (Entry 22) compared with 9% after 10 minutes. In general the oxidation reactions with FeB$^+$ appeared to proceed more slowly than those with FeB$^*$ under these conditions with larger amounts of unchanged EE$_2$ remaining after the same reaction times. Nevertheless FeB$^+$ was still an effective catalyst for oxidatively removing EE$_2$ from solution.
Oxidation reactions of EE$_2$ catalysed by SCFs using FeB$^*$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[EE$_2$] ppm</th>
<th>Mole ratio (FeB*: EE$_2$)</th>
<th>pH</th>
<th>Reaction time (minute)</th>
<th>[H$_2$O$_2$] mM</th>
<th>(%) EE$_2$ remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>9.5</td>
<td>30</td>
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<td>(1:10)</td>
<td>7.0</td>
<td>10</td>
<td>1.0</td>
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<td>10</td>
<td>1.0</td>
<td>11.0</td>
</tr>
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<td>10</td>
<td>1.0</td>
<td>5.0</td>
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<td>11</td>
<td>5</td>
<td>1.0</td>
<td>9.0</td>
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<tr>
<td>17</td>
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<td>(1:10)</td>
<td>11</td>
<td>2</td>
<td>1.0</td>
<td>14.0</td>
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</tbody>
</table>

Table 99: Summarized EE$_2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB$^*$

Oxidation reactions of EE$_2$ catalysed by SCFs using FeB$^j$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[EE$_2$] ppm</th>
<th>Mole ratio (FeB*: EE$_2$)</th>
<th>pH</th>
<th>Reaction time (minute)</th>
<th>[H$_2$O$_2$] mM</th>
<th>(%) EE$_2$ remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
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<td>7.0</td>
<td>10</td>
<td>1.0</td>
<td>71.0</td>
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<tr>
<td>19</td>
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<td>(1:10)</td>
<td>9.5</td>
<td>10</td>
<td>1.0</td>
<td>9.0</td>
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<td>(1:10)</td>
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<td>5</td>
<td>1.0</td>
<td>32.0</td>
</tr>
<tr>
<td>22</td>
<td>2.0</td>
<td>(100:1)</td>
<td>9.5</td>
<td>30</td>
<td>1.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 100: Summarized EE$_2$ oxidation reactions with SCFs (PCMS + NMP) under various condition with FeB$^j$
4.9.3 Oxidation reactions of Triclosan (TCS) using the SCFs in a beaker

A series of catalytic oxidation reactions of triclosan (TCS) was conducted in a beaker using different loadings of the catalyst FeB* (either 0.0138 µmole or 13.8 µmole, corresponding to catalyst: substrate mole ratios of 1:10 or 100:1) on SCFs. Different pHs (7, 9.5, 11.0) and reaction times (5, 10, 30 minutes) were used. In all cases the initial concentration of TCS was 2 ppm (6.91 µM), the concentration of hydrogen peroxide was 1.0 mM and the stirring speed was 1000 rpm. The SCFs were synthesised using a PCMS +NMP polymer. The conditions and results of the experiments are presented in Table 101-102.

When very large amounts of catalyst FeB* were used on the SCF (13.8 µmole, catalyst: substrate mole ratios 100:1) the TCS was completely oxidatively removed in a reaction carried out for 10 minutes at pH 9.5 (Entry 23). If the pH was maintained at 9.5, and the amount of catalyst reduced to 0.0138 mole (catalyst: substrate mole ratio 1:10), 90% of the initial TCS remained after 10 minutes (Entry 25). Clearly the TCS was more difficult to oxidise than either BPA or EE₂ under these conditions. Increasing the pH to 11.0 did not reduce the large amount of unreacted TCS (Entry 26) and reducing the pH to 7.0 shut down the oxidation altogether with 100% recovery of the TCS after 10 minutes reaction time (Entry 24). Somewhat surprisingly, when the catalyst on the SCF was changed to FeB³ at the same low level (0.0138 mole, catalyst: substrate mole ratio 1:10), the pH was 9.5 and the reaction time was 30 minutes, no unreacted TCS remained in solution. It appeared that FeB³ was a good catalyst for the oxidation of TCS under these conditions.
Oxidation reactions of TCS catalysed by SCFs using FeB*

<table>
<thead>
<tr>
<th>Entry</th>
<th>[TCS] ppm</th>
<th>Mole ratio (FeB*: TCS)</th>
<th>pH</th>
<th>Reaction time (min)</th>
<th>[H₂O₂] mM</th>
<th>(% ) TCS remaining</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.0</td>
<td>(1:10)</td>
<td>9.5</td>
<td>10</td>
<td>1.0</td>
<td>90.0</td>
</tr>
<tr>
<td>26</td>
<td>2.0</td>
<td>(1:10)</td>
<td>11</td>
<td>10</td>
<td>1.0</td>
<td>90.0</td>
</tr>
</tbody>
</table>

**Table 101: Summarized TCS oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB**

Oxidation reactions of TCS catalysed by SCFs using FeB³

<table>
<thead>
<tr>
<th>Entry</th>
<th>[TCS] ppm</th>
<th>Mole ratio (FeB*: TCS)</th>
<th>pH</th>
<th>Reaction time (min)</th>
<th>[H₂O₂] mM</th>
<th>(% ) TCS remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>2.0</td>
<td>(1:10)</td>
<td>9.5</td>
<td>30</td>
<td>1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Table 102: Summarized TCS oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB³**
4.10 Oxidative removal of real-world pollutants catalysed by SCFs using a U-tube apparatus

The same reaction system was used as in section 3.3 except this time the catalytic oxidation reactions were investigate using BPA, EE₂ and TCS.

4.10.1 Oxidation Reactions of BPA catalysed by SCFs in a U-tube apparatus

A series of catalytic oxidation reactions of BPA was conducted in a U-tube apparatus with the BPA and hydrogen peroxides separated by a SCF containing adsorbed FeB* catalyst. In all cases the initial concentration of BPA was 2 ppm (8.76 µM) and the pH of this solution was 7.0, the concentration of hydrogen peroxide was 1.0 mM and the stirring speed was 1000 rpm. The SCFs were synthesised using a PCMS+NMP polymer. Different amounts of FeB* were adsorbed (36.82, 0.263 or 0.0263 µmole, corresponding to catalyst: substrate mole ratios of 140:1, 1:1, or 1:10, respectively) onto the SCFs. The pH of the hydrogen peroxide was 7.0, 9.5 or 11.0 and different reaction times were investigated. The conditions and results of the experiments are presented in Table 103.

From the results of the reactions conducted in beakers the amount of oxidation would be expected to increase as the pH became more alkaline, the amount of catalyst increased and the time became longer. Therefore it was not surprising the reaction that was carried out with a large amount of FeB* on the SCF and the hydrogen peroxide solution buffered at pH 11.0 resulted in only 2% BPA remaining after 30 minutes (Entry 28). Reducing the amount of catalyst on the SCF so that the FeB*:BPA mole ratio was 1:1 also resulted in nearly all the BPA being oxidatively removed after 30 minutes (Entry 29). If the time for this particular reaction was reduced to 5 minutes the amount of unchanged BPA rose to 20 % (Entry 30). It is noteworthy that even after this short time most of the BPA had been oxidatively removed. If the amount of FeB* on the SCF was reduced even further so that the FeB*: BPA mole ratio was 1:10, and the pH changed to 9.5, 30% of the BPA remained unchanged after 30 minutes (Entry 31) and with this same smaller amount of catalyst if the pH was reduced to 7.0, essentially none of the BPA was oxidatively removed (Entry 32). These results show that the SCFs can perform well in catalysing the oxidative removal of BPA under these conditions.
Oxidation reactions of BPA catalysed by SCFs using FeB\(^*\) in u-tube apparatus

<table>
<thead>
<tr>
<th>Entry</th>
<th>[BPA] ppm</th>
<th>Mole ratio (FeB(^*): BPA)</th>
<th>pH (\text{H}_2\text{O}_2) side</th>
<th>pH BPA side</th>
<th>Reaction time (min)</th>
<th>[(\text{H}_2\text{O}_2)] mM</th>
<th>(%) BPA remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>2.0</td>
<td>(140:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>29</td>
<td>2.0</td>
<td>(1:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>30</td>
<td>2.0</td>
<td>(1:1)</td>
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<td>7.0</td>
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<td>7.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>100.0</td>
</tr>
<tr>
<td>32</td>
<td>2.0</td>
<td>(1:10)</td>
<td>9.5</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Table 103: Summarized BPA oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB\(^*\) in u-tube system
4.10.2 Oxidation Reactions of EE$_2$ catalysed by SCFs in a U-tube apparatus

Catalytic oxidation reactions of EE$_2$ were also conducted in a U-tube apparatus with the EE$_2$ and hydrogen peroxides separated by a SCF containing adsorbed FeB* catalyst. In all cases the initial concentration of EE$_2$ was 2 ppm (6.75 µM), the concentration of hydrogen peroxide was 1.0 mM and the stirring speed was 1000 rpm. The SCFs were synthesised using a PCMS+NMP polymer. Different amounts of FeB* were adsorbed (28.4, 20.3, 6.1, or 0.02) µmole, corresponding to catalyst: substrate mole ratios of 140:1, 100:1, 30:1, or 1:10, respectively) onto the SCFs. The pH of the hydrogen peroxide was 7.0, 9.5 or 11.0 and the substrate solution was either pH 7.0 or 9.5. Reaction times ranging from 4 – 30 minutes were used. The conditions and results of the experiments are presented in Table 104-105.

With high catalyst loadings (catalyst: substrate mole ratios of 140:1, 100:1), and with the pH of the hydrogen peroxide solution 11.0, essentially all the EE$_2$ was oxidatively removed in 30 minutes (Entries 33 and 37). Under the same conditions but with less catalyst (catalyst:substrate mole ratio of 1:10) 6% of the EE$_2$ remained after 30 minutes, 12% remained after 10 minutes, 26% after 5 minutes and 90% remained after 4 minutes reaction time (Entries 38 - 41). Clearly under these conditions close to 30 minutes was required for nearly complete oxidative removal of the EE$_2$. The pH of the hydrogen peroxide solution is very important factor in determining the efficiency of EE$_2$ removal. This is illustrated by the reaction carried out with the same low amount of FeB*, but with the pH of both the substrate and hydrogen peroxide solutions 7.0 (Entry 34). In this case no EE$_2$ was oxidatively removed at all. Even if the amount of FeB* is increased considerably so that the catalyst: substrate mole ratio is 30:1, if the pH of both reactions is 9.5, 11% of the EE$_2$ remains after 10 minutes (Entry 36).

The catalyst FeB$^1$ can also catalyse the oxidative removal of EE$_2$ when adsorbed onto the SCF in this configuration. With a catalyst:substrate mole ratio of 1:10 and the pH of the peroxide and the substrate solutions 9.5 and 7.0, respectively, all the EE$_2$ was oxidatively removed in 30 minutes (Entry 43). However, when the amount of catalyst was increased so that the catalyst:substrate mole ratio was 30:1, but the reaction time reduced to 10 minutes, 41% was recovered unchanged after a reaction time of 10 minutes (Entry 42). Clearly the reaction time is also a very important parameter for this catalyst with short times resulting in small amounts of oxidative removal of the EE$_2$. 

335
These results show that the SCFs can perform well in catalysing the oxidative removal of EE$_2$ from solution under these conditions. Example of EE$_2$ Chromatogram monitored using HPLC was observed as below:
Oxidation reactions of EE2 catalysed by SCFs using FeB* in u-tube apparatus

<table>
<thead>
<tr>
<th>Entry</th>
<th>[EE2] ppm</th>
<th>Mole ratio (FeB*: EE2)</th>
<th>pH H2O2 side</th>
<th>pH EE2 side</th>
<th>Reaction time (min)</th>
<th>[H2O2] mM</th>
<th>(%EE2) remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>2.0</td>
<td>(140:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>34</td>
<td>2.0</td>
<td>(1:10)</td>
<td>7.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>100.0</td>
</tr>
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<td>35</td>
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<td>(1:10)</td>
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<td>1.0</td>
<td>11.0</td>
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<td>1.0</td>
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</tr>
<tr>
<td>41</td>
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<td>(1:10)</td>
<td>11</td>
<td>7.0</td>
<td>5</td>
<td>1.0</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Table 104: Summary of EE2 oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB* in u-tube apparatus

Oxidation reactions of EE2 catalysed by SCFs using FeB^+ in u-tube apparatus

<table>
<thead>
<tr>
<th>Entry</th>
<th>[EE2] ppm</th>
<th>Mole ratio (FeB*: EE2)</th>
<th>pH H2O2 side</th>
<th>pH EE2 side</th>
<th>Reaction time (min)</th>
<th>[H2O2] mM</th>
<th>(%EE2) remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>2.0</td>
<td>(30:1)</td>
<td>9.5</td>
<td>9.5</td>
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<td>9.5</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 105: Summary of EE2 oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB^+ in u-tube apparatus
4.10.3 Oxidation Reactions of TCS catalysed by SCFs in a U-tube apparatus

Catalytic oxidation reactions of TCS were also conducted in a U-tube apparatus with the SCFs containing adsorbed FeB* catalyst. In all cases the initial concentration of TCS was 2 ppm (6.91 µM) with the pH of the solution was 7.0, the concentration of hydrogen peroxide was 1.0 mM and the stirring speed was 1000 rpm. The SCFs were synthesised using a PCMS+NMP polymer. Different amounts of FeB* were adsorbed (29.02, 0.21, or 0.02 µmole, corresponding to catalyst: substrate mole ratios of 140:1, 1:1. or 1:10, respectively) onto the SCFs. The pH of the hydrogen peroxide was 7.0, 9.5 or 11.0 and reaction times ranging from 5 – 30 minutes were used. The conditions and results of the experiments are presented in Table 106.

As with the oxidation reactions of the other compounds BPA and EE₂, it was found that for reactions with the pH of the hydrogen peroxide solution at 11.0, a large amount of catalyst on the SCF resulted in almost complete oxidative removal of the TCS in 30 minutes, but as the amount of catalyst decreased, more TCS remained in solution at the end of the reaction. Thus, with a catalyst: substrate mole ratios of 140:1, 1:1 or 1:10, 2%, 5% or 20% of the TCS remained unchanged, respectively (see Entries 46, 47, and 49 respectively). Decreasing the reaction time also led to less of the TCS being removed. Therefore, for the reaction with a catalyst: substrate mole ratio of 1:1 decreasing the reaction time from 30 to 5 minutes resulted in the amount of TCS not removed increasing from 5% to 25%. Similarly, for the reaction with a catalyst: substrate mole ratio of 1:10 decreasing the reaction time from 30 to 10 minutes resulted in the amount of TCS not removed increasing from 20% to 75% (Entry 50). As before, lowering the pH of the hydrogen peroxide solution also resulted in less oxidative removal of TCS. For reactions with a catalyst: substrate mole ratio of 1:10 the pH of the hydrogen peroxide 11.0, 9.5 or 7.0 the amount of TCS remaining was 20%, 30% or 100%, respectively (Entries 49, 51, 52).

These results show that the SCFs can perform well in catalysing the oxidative removal of all three real-world pollutants BPA, EE₂ and TCS when used in this configuration where the substrate solution is separated from the alkaline peroxide solution by the SCF and the pH of the substrate solution is at the environmentally relevant value of 7.0. These very important results demonstrate that the SCFs can oxidatively remove dilute solutions of these real-world contaminants from water without having to dose it with large amounts of catalyst, hydrogen peroxide or base, which was the primary goal of the research project described in this thesis.
Oxidation reactions of TCS catalysed by SCFs using FeB* in u-tube apparatus

<table>
<thead>
<tr>
<th>Entry</th>
<th>[TCS] ppm</th>
<th>Mole ratio (FeB*: TCS)</th>
<th>pH H₂O₂ side</th>
<th>pH TCS side</th>
<th>Reaction time (min)</th>
<th>[H₂O₂] mM</th>
<th>(%) TCS remaining</th>
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</thead>
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<tr>
<td>47</td>
<td>2.0</td>
<td>(1:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>48</td>
<td>2.0</td>
<td>(1:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>5</td>
<td>1.0</td>
<td>25.0</td>
</tr>
<tr>
<td>49</td>
<td>2.0</td>
<td>(1:10)</td>
<td>11.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>20.0</td>
</tr>
<tr>
<td>50</td>
<td>2.0</td>
<td>(1:10)</td>
<td>11.0</td>
<td>7.0</td>
<td>10</td>
<td>1.0</td>
<td>75.0</td>
</tr>
<tr>
<td>51</td>
<td>2.0</td>
<td>(1:10)</td>
<td>9.5</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>30.0</td>
</tr>
<tr>
<td>52</td>
<td>2.0</td>
<td>(1:10)</td>
<td>7.0</td>
<td>7.0</td>
<td>30</td>
<td>1.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 106: Summary of TCS oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB* in u-tube apparatus
4.11 Oxidative removal of real-world pollutants catalysed by SCFs using a Cross-flow apparatus

Before studies involving BPA EE₂ and TCS were carried out in the cross-flow apparatus, a blank reaction (Figure 235) was undertaken to show that orange II dye that passed through this apparatus was not bleached if no FeB* catalyst was present on the smart film. An experiment was set up in which 1.0 mM hydrogen peroxide (pH 9.5) and Orange (II) dye (pH 7) solutions were present in the two chambers of the cross-flow apparatus and were separated by a smart film that did not have any FeB* adsorbed onto it. The reaction runs for 2 hours with the dye flowing at a rate of 5.0 mL/min.

The result showed that as expected the Orange (II) dye was hardly bleached at all as it passed through the apparatus over a period of 2 hours.

Figure 235: Plot absorbance of Orange (II) with SF and 1.0 mM H₂O₂
4.11.1 Oxidative removal of BPA catalysed by SCFs using a cross-flow apparatus

Since the experiments carried out using the SCFs in the U-tube apparatus were so successful at oxidatively removing the real-world pollutants BPA, EE₂ and TCS, studies were then carried out to see whether the SCFs could be used in a cross-flow apparatus to oxidatively remove these same pollutants. This was especially important to establish because if the SCFs were ever used in practice, it is expected that this is the type of configuration that would be used and these are the type of pollutants that would be targeted for removal.

Experiments aimed at oxidatively removing BPA from solution through catalytic oxidation reactions were therefore performed in a cross-flow apparatus with SCFs (9 x 4.0 x 0.3 cm) containing adsorbed FeB⁺ catalyst. In all cases the initial concentration of BPA was 2 ppm (8.76 µM, pH 7.0), the concentration of hydrogen peroxide was 1.0 mM (pH 11.0, carbonate buffer 0.01 M) and the mesh used was a 2nd generation design. The SCFs were synthesised using a PCMS+NMP polymer. The amount of FeB⁺ adsorbed onto the SCFs was either 0.175 or 24.53 µmole. These amounts were either equivalent to or 140 times, respectively, the number of moles of TCS present in 20 mL of solution. The flow rates were either 5 or 8 mL/minute. The conditions and results of the experiments are presented in Table 107.

It was found that with a relatively small amount of catalyst FeB⁺ adsorbed onto the SCF (0.175 µmole) and a flow rate of 5 mL/minute, essentially all the BPA was oxidatively removed from solution (Entry 53). The exiting solution was sampled (3.0 mL collected) after 20 mL of BPA solution had flowed continuously at 5 mL/minute through the cross-flow apparatus. If larger amounts of catalyst were present on the SCF (24.53 µmole) and the flow rate was increased to 8 mL/minute, again all the BPA was removed from solution (Entry 54). These results showed that practically all the BPA in dilute aqueous solutions of this pollutant could in fact be removed through oxidative treatment catalysed by the SCF in a cross-flow configuration.
Oxidation reactions of BPA catalysed by SCFs using FeB* in small cross flow (9 x 4 x 0.3 cm)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[BPA] ppm</th>
<th>Amount of FeB* adsorbed on SCF (µmole)</th>
<th>pH H₂O₂</th>
<th>pH BPA</th>
<th>Flow rate (mL/min)</th>
<th>[H₂O₂] mM</th>
<th>(%) BPA remaining in the exiting solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>2.0</td>
<td>0.175</td>
<td>11.0</td>
<td>7.0</td>
<td>5.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>54</td>
<td>2.0</td>
<td>24.53</td>
<td>11.0</td>
<td>7.0</td>
<td>8.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 107: Summary of BPA oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB* in small cross-flow apparatus

Figure 236: Initial chromatogram of BPA 2ppm on the left and chromatogram of BPA remaining in exiting solution using condition entry 53 table 107 on the right
4.11.2 Oxidative removal of EE₂ catalysed by SCFs using a cross-flow apparatus

The oxidative removal of EE₂ from solution through catalytic oxidation reactions in a cross-flow apparatus with SCFs (9 x 4 x 0.3 cm) containing adsorbed FeB* catalyst were also carried out. In all cases the initial concentration of EE₂ was 2 ppm (6.75 µM, pH 7.0), the concentration of hydrogen peroxide was 1.0 mM (pH 11.0, carbonate buffer 0.01 M) and the mesh used was a 2nd generation design. The SCFs were synthesised using a PCMS+NMP polymer. The amount of FeB* adsorbed onto the SCFs was either 10.8, or 18.9 µmole. These amounts were equivalent to either 80 or 140 times, respectively, the number of moles of BPA present in 20.0 mL of solution. The flow rates were either 5 or 8 mL/minute. All the conditions and results of the experiments are presented in Table 108.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[EE₂] ppm</th>
<th>Amount of FeB* adsorbed on SCF (µmole)</th>
<th>pH H₂O₂</th>
<th>pH EE₂</th>
<th>Flow rate (mL/min)</th>
<th>[H₂O₂] mM</th>
<th>(%) EE₂ remaining in exiting solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>2.0</td>
<td>10.8</td>
<td>11.0</td>
<td>7.0</td>
<td>5.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>56</td>
<td>2.0</td>
<td>10.8</td>
<td>11.0</td>
<td>7.0</td>
<td>8.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>57</td>
<td>2.0</td>
<td>18.9</td>
<td>11.0</td>
<td>7.0</td>
<td>5.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>58</td>
<td>2.0</td>
<td>18.9</td>
<td>11.0</td>
<td>7.0</td>
<td>8.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 108: Summary of EE₂ oxidation reactions with SCFs (PCMS +NMP) under various condition with FeB* in small cross-flow apparatus
The results show that with higher catalyst loading (18.9 μmole) on the SCF and flow rates of either 5 or 8 mL/minute essentially all the EE$_2$ was oxidatively removed from the exiting solution (Entries 57 and 58). Even with lower a smaller catalyst loading of (10.8 μmole) on the SCF essentially all the EE$_2$ was oxidatively removed from the exiting solution at the flow rates of 5 or 8 mL/minute (Entries 55 and 56). This indicated that when operating in a cross-flow configuration the SCFs were very effective at catalysing the oxidative removal of EE$_2$ from solution.
4.11.3 Oxidative removal of TCS catalysed by SCFs using a cross-flow apparatus

Finally, the removal of TCS from solution through catalytic oxidation using a cross-flow apparatus with SCFs (9.0 x 4.0 x 3.0 cm) containing adsorbed FeB* catalyst was also explored. In both cases the initial concentration of TCS was 2 ppm (6.91 µM, pH 7.0), the concentration of hydrogen peroxide was 1.0 mM (pH 11.0, carbonate buffer 0.01 M) and the mesh used was a 2nd generation design. The SCFs were synthesised using a PCMS+NMP polymer. The amount of FeB* adsorbed onto the SCFs was either 0.138 µmole, or 19.4 µmole. These amounts were either equivalent to or 140 times, respectively, the number of moles of TCS present in 20.0 mL of solution. The flow rates were either 5 or 8 mL/minute. All the conditions and results of the experiments are presented in Table 109.

The results show that with either a relatively large amount of catalyst present (19.4 µmole) and a high flow rate of 8 mL/minute, or with a much smaller amount of catalyst (0.138 µmole) and the lower flow rate of 5 mL/minute essentially all the TCS was oxidatively removed from solution (Entries 59 and 60, respectively). Clearly, TCS could also be removed from solution using the SCFs in a cross-flow apparatus.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[TCS] ppm</th>
<th>Mole ratio (FeB*: BPA)</th>
<th>pH H₂O₂</th>
<th>pH BPA</th>
<th>Flow rate (mL/min)</th>
<th>[H₂O₂] mM</th>
<th>(%) TCS remaining in exiting solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>2.0</td>
<td>(1:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>5.0</td>
<td>1.0</td>
<td>&lt; 3.0</td>
</tr>
<tr>
<td>60</td>
<td>2.0</td>
<td>(140:1)</td>
<td>11.0</td>
<td>7.0</td>
<td>8.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 109: Summary of TCS oxidation reactions with SCFs (PCMS+NMP) under various condition with FeB* in small cross-flow apparatus
In conclusion, investigations were carried out into the oxidative removal of the three pollutants BPA, EE₂ and TCS, using SCFs in a cross-flow apparatus. These three compounds, which have all be found in numerous drinking water supplies, are recognised as compounds of concern because they have significant endocrine disrupting properties. They are therefore “real world” pollutants. The SCF in the cross-flow apparatus separates the alkaline hydrogen peroxide oxidant solution from the dilute solution of the pollutant which is at the environmentally relevant pH of 7.0. The SCF also contains the oxidation catalyst, FeB*. It was found that when used in this configuration, the SCFs could very effectively catalyse the oxidative removal of each of these pollutants from aqueous solution. The results are very important because they demonstrate that the SCFs in this practical configuration can achieve essentially complete removal of the real world pollutants BPA, EE₂ and TCS without gross contamination of the solution with catalyst, base or hydrogen peroxide. Clearly, more extensive studies of these reactions are needed. In particular it will be important to optimise the conditions so that the maximum volume of contaminated solution can be treated quickly with the minimum use of hydrogen peroxide, base and catalyst. The results from the experiments with organic dyes (which can be considered to be surrogate pollutants) in the cross-flow apparatus suggest that using low concentrations of hydrogen peroxide at weakly alkaline pH will probably maximise catalyst lifetime and turn-over-numbers. This will be an important factor when treating large volumes of water that

![Figure 238: Initial chromatogram of TCS 2ppm on the left and chromatogram of TCS remaining using condition entry 60 table 110 on the left](image)
contain very small amounts of pollutants. Future work should also involve determining what oxidation products are formed in these reactions and determination of the endocrine disrupting potentials of these products as well as studies of a wider range of known problematic pollutants.
4.12 Yeast estrogen assay (YES) tests

Preliminary YES tests were carried out on solutions of BPA and EE$_2$ that had been oxidatively treated with hydrogen peroxide in the presence of SCFs containing FeB$^*$ (0.0135 μmoles) catalyst in reaction using a simple beaker configuration. Full details are provided in the experimental section 4.1.3.11.

The YES results showed that the solutions of EE$_2$ and BPA after oxidative treatment had very much less estrogenic activity than the reference compound E$_2$. While the YES test is not a conclusive test for estrogenicity these results indicate that the oxidised products formed from these compounds most probably actually do have very little estrogenicity.

![Graph showing YES test results for EE$_2$ and BPA with E$_2$ as reference compound](image)

Figure 239: YES test for EE$_2$ and BPA with E$_2$ as reference compound
4.1.3 Experimental Procedures

4.1.3.1 Typical experiment involving oxidation of EE$_2$ by hydrogen peroxide catalysed by a SCF containing FeB* in a beaker.

In a typical experiment a carbonate/bicarbonate buffer solution (8.5 mL, 0.01 M, pH 9.5), was added to a beaker, H$_2$O$_2$ solution (0.1 mL, 0.2 M) was added followed by EE$_2$ solution (11.4 mL, 11.83 µM) and the total volume made up to 20.0 mL by adding more of the buffer solution. The resulting concentration of EE$_2$ was 2 ppm (6.76 µM) and H$_2$O$_2$ was 1.0 mM. With the stirring speed was maintained at 750 rpm a circular SCF 35 mm in diameter (the SCF was prepared from five nominally 50 µm coatings of a PCMS polymer cross-linked with 1,6-diaminohexane on a polypropylene backing) containing adsorbed FeB* catalyst (4.05 µmole) was then placed in the solution so that it sat on the supporting wire loop. Mole ratios of H$_2$O$_2$: EE$_2$: FeB* were either 20,000: 135: 1.35 or 200: 1.35: 40.5. This was taken as time zero for the reaction. After 30 minutes the SCF was removed, catalase (1 mg) was added to the solution which was stirred for a further 30 minutes. Peroxide test strips were used to confirm all the hydrogen peroxide was destroyed after this time. The solution was then acidified to pH 3.5 by addition of 4 M HCl and left to stand a further 1 min. The solution was then filtered through a GF 2 glass fibre filter paper and the organic material collected by passing through solid phase extraction cartridge (200 mg hydrophilic-lipophilic balance (HLB) cartridge from Water Corp) at 10 mL per minute. The cartridge was preconditioned with 10 mL mili-Q water followed by 10 mL methanol before use. The cartridge was then eluted with 10 mL methanol at a flow rate of 4 mL/min. The eluate was collected and the organic solvent was evaporated to dryness by rotatory evaporation and further dried under nitrogen. Methanol (0.50 mL) was added to dissolve the residue and the solution made up to 1.00 mL with mili-Q water and filtered using a nylon membrane filter (0.22 µm pore size/13 mm diameter) and then analysed by HPLC using a Shimadzu LC-20AT instrument.
4.1.3.2 Typical experiment involving oxidation of BPA by hydrogen peroxide catalysed by a SCF containing FeB\(^*\) in beaker.

In a typical experiment the procedure described above for the oxidation and analysis of EE\(_2\) was followed except that BPA (2 ppm, 8.76 µM) was used as substrate.

4.1.3.3 Typical experiment involving oxidation of TCS by hydrogen peroxide catalysed by a SCF containing FeB\(^*\) in beaker

In a typical experiment the procedure described above for the oxidation and analysis of EE\(_2\) was followed except that TCS (2 ppm, 6.91 µM) was used as substrate.

4.1.3.4 Conditions for HPLC analysis of EE\(_2\)

The HPLC instrument used was a Shimadzu LC-20AT HPLC with an SPL-20A UV-vis detector;\(^{268}\) the column (stationary Phase) was an Accucore XL C18, 150mm x 4.6 mm x 4 µm column; the Guard Column, an Accucore XL C18 4 UM unit; the Mobile Phases used were Solvent A: mili-Q water acidified with formic Acid (0.1%), Solvent D, a mixture of methanol: acetonitrile (1:3). The column temperature was 30°C; the Detector was a diode array detector (DAD) set at 230 and 217 nm\(^{269}\); Flow rate, 0.667 mL/min; Injection volume, 40 µL; Isocratic run, \(t = 0\) min (40% mobile phase D, 60% mobile phase A) \(t = 21\) min (40% mobile phase D, 60% mobile phase A) \(t = 22\) min, stop elution.

4.1.3.5 Conditions for HPLC analysis of BPA

The same HPLC instrument, column, guard column, and solvents A and D as above for the EE\(_2\) analysis were used. Other conditions were: column temperature, 30°C; Detector, diode array detector (DAD) set at 230 and 280 nm\(^{264}\); Flow rate, 0.667 mL/min; Injection volume, 40 µL; Isocratic run, \(t = 0\) min (40% mobile phase D, 60% mobile phase A) \(t = 21\) min (40% mobile phase D, 60% mobile phase A), \(t = 22\) min, stop elution.

4.1.3.6 Condition for HPLC analysis for TCS

The same HPLC instrument, column, guard column, and solvents A and D as above for the EE\(_2\) analysis were used. Other conditions were: Column temperature, 30°C; Detector, diode array detector (DAD) at 230 and 280 nm\(^{270}\); Flow rate, 0.667 mL/min; Injection volume, 40 µL; eluent conditions, gradient run, \(t = 0\) min (55% mobile phase D, 45% mobile phase A), \(t = 22\) min (55% mobile phase D, 45% mobile phase A), \(t = 22\) min, stop elution.
4.1.3.7 Oxidative destruction of EE$_2$ with hydrogen peroxide using a SCF in the U-tube apparatus

In a typical experiment a circular (35 mm diameter) SCF was fixed between the arms of the 3 cm diameter U-tube. The SCF was prepared from five nominally 50 µm coatings of a PCMS polymer cross-linked with 1,6-diaminohexane on a polypropylene backing and contained FeB* (20 nmole). The substrate solution volume was 30 mL and contained EE$_2$ (2 ppm, 6.76 µM) in deionized water (pH 7.0). The oxidant solution contained H$_2$O$_2$ (1.0 mM) in carbonate/bicarbonate buffer (100 mL, 0.01 M, pH 11.0). The mole ratio of EE$_2$ to FeB* was 1:10. The stirring speed of both solutions was 1000 rpm and the time of the reaction was 30 minutes. After this time the substrate solution was removed, treated and analysed by HPLC as described above in section 4.1.3.1.

4.1.3.8 Oxidative destruction of BPA with hydrogen peroxide using a SCF in the U-tube apparatus

The same experimental procedure for the oxidation reaction was used as that described above in section 4.1.3.7 except that the substrate solution contained BPA (2 ppm, 8.76 µM) in deionized water (pH 7.0) and the SCF contained FeB* (26 nmole). After the oxidation reaction was complete the substrate solution was removed, treated and analysed by HPLC as described above in section 4.1.3.2.

4.1.3.9 Oxidative destruction of TCS with hydrogen peroxide using a SCF in the U-tube apparatus

The same experimental procedure for the oxidation reaction was used as that described above in section 4.1.3.8 except that and the substrate solution contained TCS (2 ppm, 6.91 µM) in deionized water (pH 7.0) and the SCF contained FeB* (21 nmole). After the oxidation reaction was complete the substrate solution was removed, treated and analysed by HPLC as described above in section 4.1.3.3.

4.1.3.10 Oxidative destruction of orange (II), BPA and TCS with hydrogen peroxide using a SCF in the cross-flow apparatus

In a typical experiment the SCF was clamped between the two halves of the cross-flow apparatus. The SCF was prepared from five nominally 50 µm coatings of a PCMS polymer cross-linked with 1,6-diaminohexane on a polypropylene backing and contained FeB* (20 nmole). The hydrogen peroxide oxidant solution (1.0 mM) in carbonate/bicarbonate buffer (0.01 M, pH 11.0) filled the bottom chamber of the cross-flow apparatus and was connected by
tubes to a reservoir that could be adjusted in height. An open acrylic support was placed in this chamber to support the SCF. The hydrogen peroxide reservoir was raised 20 cm above the SCF in the cross-flow apparatus. The resulting small hydrostatic head produced a pressure differential across the SCF that caused the perfusion of the hydrogen peroxide through the film. The solution containing the orange (II) substrate (50 µM) in deionized water (pH 7.0) was then pumped by a peristaltic pump at a rate of 5.0 mL/minute through the other chamber of the cross-flow apparatus. A plastic mesh in this chamber sat on top of the SCF to induce turbulence to the flow of the orange (II) solution. The dimensions of the SCF exposed to the flowing orange II solution was 4 cm x 9 cm. Under these conditions the absorbance of the orange II solution entering the cross-flow apparatus (initial absorbance) was 1.05 and the absorbance of the solution exiting the apparatus was 0.15. This indicates that approximately 85% of the dye was oxidised during this one pass through the apparatus. Therefore, under these conditions, the 36 cm² SCF can treat 5 mL of solution per minute.

The above experiment was repeated under the same conditions except that the substrates used were either EE₂ (2 ppm, 6.76 µM), BPA (2 ppm, 6.76 µM) or TCS (2 ppm, 6.76 µM) in deionized water (pH 7.0). These solution exiting the apparatus was collected and analysed as described above in section 4.1.3.1, 4.1.3.2 and 4.1.3.3, respectively.

4.1.3.11 Procedure used to carry out the YES test on oxidatively treated EE₂ solution

Sample preparation EE₂

An experiment involving the oxidative removal of EE₂ by hydrogen peroxide and catalysed by a SCF in a beaker as described in section 4.1.3.1 above was carried out. The experimental details were: total volume of solution 20 mL, H₂O₂ (1.00 mM, 0.12 mL of, 0.165 M stock solution), EE₂ (2ppm, 6.75 µM, 13.5 µM stock solution), FeB* (9.0 µg) (catalyst:EE₂ mole ratio1:10) with stirring speed 550 rpm in carbonate buffer pH 9.5. The reaction was run for 30 min. After this time approximately 1mg of catalase was added to completely destroy the H₂O₂ and the stirring continued for another 30 min to ensure no peroxide was present with a peroxide test strip. The solution was then neutralised with 4 M HCl to give pH ca. 7 which is suitable for a yeast/bacteria medium. The reaction solution was then filtered through a GF2 glass fibre filter paper and a 0.10 mL aliquot taken from the filtered solution and diluted to 1.00 mL using Mili-
Q water in HPLC glass vial to give a final concentration 0.675 µM. A series of 10 dilutions per sample was prepared in triplicate and therefore in total 30 samples was prepared per analysis.

**Sample preparation for BPA**

An experiment involving the oxidative removal of EE$_2$ by hydrogen peroxide and catalysed by a SCF in a beaker as described in section 4.1.3.2 above was carried out. The experimental details were: total volume of solution 20 mL, H$_2$O$_2$ (1.00 mM, 0.12 mL of, 0.165 M stock solution), EE$_2$ (2ppm, 8.76 µM, 13.5 µM stock solution), FeB* (11.7 µg) (catalyst:EE$_2$ mole ratio 1:10) with stirring speed 550 rpm in carbonate buffer pH 9.5. The reaction was run for 30 min. After this time approximately 1mg of catalase was added to completely destroy the H$_2$O$_2$ and the stirring continued for another 30 min to ensure no peroxide was present with a peroxide test strip. The solution was then neutralised with 4 M HCl to give pH ca. 7 which is suitable for a yeast/bacteria medium. The reaction solution was then filtered through a GF2 glass fibre filter paper and a 0.10 mL aliquot taken from the filtered solution and diluted to 1.00 mL using Mili-Q water in HPLC glass vial to give a final concentration 8.76 µM. A series of 10 dilutions per sample was prepared in triplicate and therefore in total 30 samples was prepared per analysis.

**4.1.3.12 Preparation of EE$_2$ stock solution**

A stock solution of EE$_2$ was prepared by dissolving EE$_2$ (1.0 mg, M, 296.17) with 0.25 mL AR grade methanol in a 25 mL beaker. This mixture was quantitatively transferred to 25 mL volumetric flask containing 150 mL deionized water. The beaker was rinsed few times with deionized water and transfer to volumetric flask up to the mark. The solution was heated up to 30°C for at least 3 hours to ensure all EE$_2$ completely dissolved with occasional mixing. EE$_2$ solubility in water 9.2 ± 0.09 mg/L$^{271}$.

**4.1.3.13 Preparation of BPA stock solution**

A stock solution of EE$_2$ was prepared by dissolving BPA (3.2 mg, M, 228.29) with 0.25 mL AR grade methanol in a 25 mL beaker. This mixture was quantitatively transferred to 25 mL volumetric flask containing 150 mL deionized water. The beaker was rinsed few times with deionized water and transfer to volumetric flask up to the mark. The solution was heated up to 30°C for at least 3 hours to ensure all BPA completely dissolved with occasional mixing. BPA solubility in water (300 ± 5) mg/L$^{271}$. 
4.1.3.14 Preparation of TCS stock solution

A stock solution of TCS was prepared by dissolving TCS (1.0 mg, \( M_r = 289.54 \)) with 0.25 mL AR grade methanol in a 25 mL beaker. This mixture was quantitatively transferred to 25 mL volumetric flask containing 150 mL deionized water. The beaker was rinsed few times with deionized water and transfer to volumetric flask up to the mark. The solution was heated up to 30°C for at least 3 hours to ensure all TCS completely dissolved with occasional mixing. TCS solubility in water 10.0 mg/L\(^{272}\).

4.1.3.14 YES protocol

The yeast used was a modified version of a receptor mediated \( \beta \)-galactosidases which was prepared by culture overnight in synthetic complete media lacking uracil and tryptophan (SC-UW) at 30 °C in a shaking water bath. The next morning the cells were diluted back to an optical density of 0.08 at 600 nm (O.D.600) and incubated in a shaking water bath at 30 °C until the culture reached and O.D. 600 of 0.1. If the samples were measured directly (Fig below, left side) aliquots (1 mL) of the yeast culture in log phase growth were transferred into 14 mL snap-cap tubes. The cells were then harvested by centrifugation at 2000 rpm for 2 min. and suspended in 1 mL of SC-UW prepared by mixing 750 μl of oxidised substrate solution with 250 μL of 4× concentrated SC-UW for each assay to be performed. The cultures were then incubated at 30 °C with shaking for 2 h. 100 μl from each culture was then transferred to an opaque 96-well plate in preparation for the addition of substrate. It is important to note that, in this case, the waste water oxidised substrate sample was extracted, concentrated, or sterilized in any way. For all assays a 17β-estradiol standard curve was performed in parallel. Standards in this case were prepared by diluting 17β-estradiol into distilled, deionized water and treating it in the same manner as the oxidised substrate samples. In the event that extracted and/or concentrated samples were being assayed (Fig. 1, right side) the growing culture was then aliquoted into an opaque 96-well plate at 100 ul per well. The concentrated samples or hormone standards in ethanol vehicle were then added directly to the wells and the plate was incubated at 30 °C for 2 h. The amount of ethanol added never exceeded 1% of the total culture volume. After the 2 h incubation in the presence of hormone 100 μl of Tropix Gal-Screen in Buffer B (Applied Biosystems, Foster City, CA) was added to each well and the plate was incubated for an additional 2 h at room temperature. The hormone-induced chemiluminescent signal was then measured on a Luminoskan Ascent microplate luminometer (Thermo Fisher Scientific Inc., Waltham, MA)\(^{273}\).
Overall YES protocol simplified in the scheme below:

1. Inoculate yeast into 10 ml SC-UW and grow overnight at 30°C with shaking.
2. Dilute culture back to an optical density of 0.08 at 600 nm and allow to reach log phase growth.
3. Direct measure of non-extracted samples:
   - Transfer 1 ml of culture into conical tube.
   - Centrifuge and remove supernatant.
   - Add 750 μl wastewater and 250 μl 4 x SC-UW. Incubate at 30°C (2 hours).
4. Extracted/concentrated samples:
   - Transfer 100 μl/well of culture into opaque 96-well plate.
   - Add 1 μl/well standards or conc. contaminates. Incubate at 30°C (2 hours).
   - Transfer 100 μl/well to opaque 96-well plate.
   - Add 100 μl/well Gal-Screen Reagent. Incubate at rm. temp. (2 hours).
5. Microplate Luminometer.
5.0 Conclusions

This thesis describes the synthesis of a chloromethylstyrene (CMS) polymer that was made through a homopolymerization method and the use of this polymer to successfully prepare a thin membrane film by casting on a backing, heat curing and cross-linking. The properties of this polymer film was then altered by applying a series of functionalization processes to form a “smart film” that contained positively charged quaternary ammonium groups and long alkyl chain “brushes”. Other related polymers were also prepared through the copolymerization of CMS and styrene (1:1 ratio) or emulsion polymerisation of CMS. The moderately reproducible formation of polymers by the preferred first method was confirmed by monitoring simple polymer parameters such as viscosity, average molar mass and polydispersivity index (PDI) which were determined through GPC and rheometer measurements. The nature of the surface of the functionalised smart film, as well as the distribution of polymer on the backing material was determine using SEM, TEM, optical microscopy, and confocal laser microscopy using Imaris 3D software.

Of the methods of polymer synthesis investigated, the three that gave the best smart catalytic films (designated PCMS + NMP, PCMS + (0.5%) DVB and Copolymer + (0.5%) DVB) based on preliminary experiments involving permeability and catalytic bleaching tests were chosen for further study. The performance of the smart catalytic films (SCFs) was measured using three different configurations. These were catalytic oxidation reactions carried out in (i) a beaker where the hydrogen peroxide, base, oxidant and substrate were mixed together and maintained in contact with the SCF), (ii) a “U-tube” apparatus where the hydrogen peroxide and base were separated from the substrate solution by the SCF, and (iii) a “cross-flow” apparatus where again the hydrogen peroxide and base were separated from the substrate solution by the SCF but the substrate solution slowly flowed over the SCF while the hydrogen peroxide solution remained static. In configurations (ii) and (iii) a small positive pressure was applied to the hydrogen peroxide solutions by holding the reservoir of this solution 10-30 cm above that of the substrate solution. This provided the driving force for the hydrogen peroxide to permeate through the SCFs. In the three configurations the performance of the SCFs were monitored as a number of different variables were changed. These included the backing material, film thickness, catalyst loading, types of catalysts, pH, stirring rates, different buffer
systems, different concentrations of hydrogen peroxide, nature of the dyes used as substrates, nature of “real-world” substrates.

The result showed that in all three configurations the SCFs successfully catalysed the bleaching (oxidation) of the dyes orange II, pinacyanol chloride, safranine O and phenolphthalein. Experiments also showed that the “real-world” endocrine disrupting compounds (EDCs) BPA, EE₂ and TCS can be oxidatively destroyed using the SCFs in either the U-tube apparatus or cross-flow apparatus. As a result, this indicates it should be possible to oxidatively remove these, other related organic pollutants and EDCs in practical water treatment applications without having to dose the entire body of water with catalyst, base and chemical oxidants. Moreover with this technology, when the catalyst on the SCFs becomes inactivated, it can be simply replaced by contacting the SCF with an aqueous solution of the catalyst. This “regeneration” occurs without any measurable reduction in the performance of the SCFs. Most of the catalytic oxidation work described in this thesis used the iron-TAML compounds FeB∗ or FeB⁺ as the oxidation catalysts on the SCFs. Compared to situations where these compounds are used as homogeneous catalysts, it was found that when adsorbed onto the SCFs they had considerably extended life-times and furthermore, oxidations using low concentrations of hydrogen peroxide (ca. 0.01 mM) and relatively low pHs (ca. 8.0 – 8.5) still proceeded at reasonable rates and resulted in greatly extended catalyst life-times. It is anticipated that commercial application of this technology could be less expensive and more efficient to run municipal water treatment than alternative technologies such as ozonation and GAC (granular activated carbon).

These studies have produced the foundations for a large number of future studies. Among these are: further development of the polymer so that better control of permeability towards hydrogen peroxide is obtained, exploration of the use of different brush materials and catalyst anchoring strategies, more detailed studies of the rates of substrate oxidation by the SCFs and catalyst decomposition on the SCFs, studies of the oxidation products formed by the catalytic oxidation of real-world pollutants and measurement of the endocrine disrupting properties and toxicity of these products. The application of the SCFs to other catalytic reactions is also a potential area for future studies.
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