

Functional Cellulosic Materials in Precision Oil-Water Separation for Fatberg Point Source Control

By

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A dissertation submitted to Imperial College London for the degree of
Doctor of Philosophy

April 2024

Declaration of Originality

I hereby declare that this thesis and the work reported here is result of my own work. Any information derived from published and unpublished work of other researchers have been acknowledged in the text and references provided.

The contents of chapter 5 (and some contents in Chapter 3) were published in Tsaone Gosiamemang and Jerry Y. Y. Heng, Simple one-pot fabrication of durable superhydrophobic cotton wool using octadecyltrimethoxysilane modified silica-sol for oil-water separation, *Separation and Purification Technology*, 2024, Volume 336, Pages 1383-5866.

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Dedication

To my beloved mother, *Oarabile Gosiamemang*, your memory will forever be cherished, and your legacy will live on in my heart.

Acknowledgements

Firstly, I want to thank God, whose infinite grace and guidance have been the cornerstone of my doctoral journey. I am deeply grateful to Professor Jerry Heng for giving me the chance to join his esteemed research group and for his steadfast guidance and assistance throughout my doctoral journey. Professor Jerry Heng has been an exceptional mentor, offering invaluable insights, unwavering support, and encouragement every step of the way. His expertise, dedication, and commitment to fostering an environment of academic excellence have been truly inspiring. In particular, I am thankful for Professor Jerry Heng's patience, understanding, and willingness to go above and beyond in ensuring my academic and personal growth. His mentorship has not only shaped my research endeavours but has also instilled in me a profound sense of confidence and determination. I would also like to thank Professor Camille Petit for her invaluable support during my research journey and her guidance in refining my CV. Our fruitful discussions have been enlightening, and I have learned a great deal from her expertise and insights. Much appreciation to Dr. Umang Shah for his mentoring, assistance with the tablet press and for providing teaching opportunities that kept me engaged and facilitated my learning in the field of teaching.

I would also like to extend my heartfelt gratitude to my research group colleagues for their support throughout my PhD journey. To each member of the research group, your encouragement, collaboration, and shared experiences have been invaluable. Your diverse perspectives, insights, and willingness to lend a helping hand have not only enriched my research but have also made this academic endeavour immensely fulfilling. I am particularly grateful for the countless discussions, brainstorming sessions, and collaborative efforts that we shared, in particular with Ethan Errington, Aobakwe Seanneng, Isha Bade, Dr. Vivek Verma, Dr. Mingxia Guo and Deniz Etit. Your collective knowledge and expertise have been instrumental in overcoming challenges and achieving milestones. I want to offer my sincere thanks to Dr. Vikram Karde for his invaluable assistance with Inverse Gas Chromatography training and sample analysis during the initial stages of my

research. Additionally, I am deeply thankful to Dr. Wenqian Chen for his guidance and support with SEM analysis and training in silica synthesis during my first year of PhD study. I also extend my appreciation to Dr. Mingxia Guo for her assistance with XRD characterisation. Their expertise and generosity have significantly enriched my research journey. I am truly privileged to have had the opportunity to work alongside such talented and dedicated individuals. Your support has not only contributed to the success of my PhD but has also left an indelible mark on my personal and professional growth. Additionally, I extend many thanks to the support staff in the Department of Chemical Engineering for their invaluable assistance during my PhD.

I want to take a moment to express my deepest appreciation to my family for their unwavering support throughout my academic journey. I am truly grateful for the countless sacrifices they have made to ensure my success, whether it was offering a listening ear, providing words of encouragement, or simply being there for me when I needed it most. Your unwavering support has been the cornerstone of my academic achievements, and I am profoundly thankful for your constant presence and belief in my abilities. To my aunts, Kesegofetse Chabaesele (and her husband, Oarabile Modise) and Sammy Ndlovu-Dawika, your unwavering belief in my abilities, even during the most challenging times, has given me the courage to persevere and pursue my dreams. I am grateful for the strong support, laughter, and good times shared with my friends, both in the UK and back home in Botswana, throughout my PhD journey. I want to express my sincere gratitude to Mbabi Tema for her constant moral support and uplifting words during the challenging phases of my PhD journey. Additionally, I deeply appreciate her assistance with proofreading of the thesis. I also would like to thank Government of Botswana for their support throughout my academic journey, from my A-Levels to the completion of this PhD (TR No.: 168859). ***‘Last but not least, I want to thank me.’ Without my own determination, hard work and resilience, this achievement would not have been possible.***

Abstract

Fatbergs, composed of congealed fat, oil, grease, wet wipes, and other non-biodegradable waste, pose a multitude of problems for urban areas. These conglomerations obstruct sewer systems, causing backups and overflows that result in sewage spills onto streets, homes, and water bodies, leading to environmental contamination and health hazards. Additionally, their removal requires significant resources, including specialised equipment and manpower, increasing maintenance costs for sewage infrastructure. Despite existing solutions such as the use of grease interceptors, the fatberg issue persists. This study explores the efficacy of superhydrophobic/superoleophilic and superhydrophilic/superoleophobic cellulose-based materials in extracting fats, oils, and grease (FOGs) from wastewater before its discharge into sewers. By eliminating FOGs from wastewater that contribute to fatberg formation, these materials offer a promising solution. Superhydrophobic materials were synthesised using the silica sol-gel method, employing octadecyltrimethoxysilane (ODTMS) as a surface modifier, through both a two-step post-grafting process and a one-pot synthesis approach. The resulting superhydrophobic cotton exhibited superior water contact angle (WCA) ($> 154^\circ$) and demonstrated remarkable durability even in harsh chemical environments, including laundering tests. Furthermore, the modified cotton demonstrated outstanding oil-water separation efficiency, exceeding 99% for immiscible oil-water mixtures, and achieved over 90% efficiency for surfactant-free oil-in-water emulsion separation. For effective separation of both surfactant-free and surfactant-stabilised emulsions, superhydrophilic cellulose-based materials were developed via dip coating in a solution of Polyethylenimine (PEI) and polyvinylpyrrolidone (PVP) polymers. These materials, including cotton wool, tissue paper, and used tea bags, exhibited excellent separation performance, achieving efficiencies exceeding 99% with high fluxes exceeding $8000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for pressure-driven filtration. Additionally, the modified cotton displayed enhanced stability, maintaining separation efficiencies above 97% even after 20 reuse cycles. In conclusion, this study demonstrates that sorption and filtration-based separation methods,

employing superhydrophilic and superhydrophobic materials, offer viable solutions for removing FOGs from wastewater and mitigating fatberg formation.

Publications

1. **Tsaone Gosiamemang**, Jerry Y.Y. Heng, Sodium hydroxide catalysed silica sol-gel synthesis: Physicochemical properties of silica nanoparticles and their post-grafting using C8 and C18 alkyl-organosilanes, *Powder Technology* 2023, Volume 417, 118237
2. **Tsaone Gosiamemang**, Jerry Y.Y. Heng, Simple one-pot fabrication of durable superhydrophobic cotton wool using octadecyltrimethoxysilane modified silica-sol for oil-water separation, *Separation and Purification Technology* 2024, Volume 336, 126185.
3. **Tsaone Gosiamemang**, Robert V. Law, Jerry Y.Y. Heng, Effects of base catalyst on the physicochemical properties and surface reactivity of silica nanoparticles. *In preparation*.
4. **Tsaone Gosiamemang**, Ethan Errington, Curran Kalha, Deniz Etit, Anna Regoutz, Jerry Y.Y. Heng, Room temperature acid catalysed silanisation of silica nanoparticles in non-polar organic solvents. *In preparation*.
5. **Tsaone Gosiamemang**, Jerry Y.Y. Heng, Superwetting materials as an alternative solution to addressing fatbergs through FOGs removal from wastewater. *In preparation*.
6. Ke Jing Toh, Afiqah K B Alias, **Tsaone Gosiamemang**, Jerry Y. Y. Heng, Superhydrophobic Cotton wool with switchable wettability for oil-water separation. *In preparation*.

Table of Contents

Declaration of Originality	2
Copyright Declaration.....	3
Dedication	9
Acknowledgements	10
Abstract	7
Publications.....	9
Table of Contents	10
List of Tables.....	15
List of Figures	16
Chapter 1. Introduction	22
1.1. Background and Motivation	22
1.2. Project Objectives.....	24
1.3. Thesis Structure	25
References	26
Chapter 2. Scientific Background and Literature Review	28
2.1. The Origins of Fatbergs and Their Formation Mechanisms	28
2.1.1. Sources of Free Fatty Acids.....	29
2.1.2. Calcium Ions	31
2.1.3. Sewer Reaction Conditions.....	32
2.2. Current Methods of Mitigating FOG Deposits.....	33
2.2.1. Control at the Source Point.....	33
2.2.2. Control in the Sewers.....	35
2.3. Limitations of the Current Solutions	35
2.4. Utilisation of FOGs in Biodiesel Production	36
2.5. Adsorption and Filtration-based Separation.....	37
2.5.1. Adsorption Kinetics	37
2.5.2. Packed Bed Adsorption	38
2.5.3. Filtration Process	40

2.6. Sorption and Filtration in Oil-water Separation	41
2.6.1. Types of Oily Wastewater	41
2.7. Superhydrophobic Materials	42
2.7.1. Synthesis of Superhydrophobic Powders and their Application in Oil-water Separation.....	44
2.7.2. Durability	48
2.7.3. Reusability	48
2.7.4. Large-scale Superhydrophobic Sorbents/Filters.....	49
2.8. Superhydrophilic and Superamphiphilic Materials.....	57
2.9. Materials with Switchable Wettability	59
2.10. Summary	61
References	61
Chapter 3. Methodology.....	72
3.1. Materials.....	72
3.2. First Pre-treatment Stage of Cellulosic Materials	73
3.3. Characterisation of Samples	73
3.3.1. Morphology	73
3.3.2. Chemical Analysis	73
3.3.3. Thermal Properties.....	74
3.3.4. Wetting Properties	75
3.3.5. Surface Energy Analysis.....	75
3.4. Durability Study	78
3.5. Water Sorption	79
3.6. Oil-water Separation.....	79
3.6.1. UV-Vis Spectrometer	80
3.6.2. Total Organic Carbon (TOC) Analyser	82
References	82
Chapter 4. Preliminary Experiments Using Chicken Eggshell Waste and Silica Nanoparticles ...	84
Abstract	84
4.1. Introduction	84
4.2. Materials and Methods	86

4.2.1. Materials	86
4.2.2. Two-step Synthesis of Modified Silica Nanoparticles	86
4.2.3. One-pot Synthesis of Superhydrophobic Silica Particles	87
4.2.4. Mechanochemical Synthesis of Superhydrophobic Eggshell Powder.....	87
4.2.5. Characterisation of the Samples	88
4.2.6. Oil-water Separation	88
4.3. Results and Discussions	88
4.3.1. Morphology and the Wettability of the Prepared Samples.....	88
4.3.2. Thermal Analysis	91
4.3.3. Application for Oil-water Separation	93
4.4. Conclusions	96
References	96
Chapter 5. Two-step Synthesis of Superhydrophobic Cotton for FOG Recovery from Wastewater.....	99
Abstract	99
5.1. Introduction	99
5.2. Materials and Methods	100
5.3.1. Materials	100
5.3.2. Cotton Pre-treatment.....	101
5.3.3. Synthesis of Silica-loaded Cotton.....	101
5.3.4. Hydrophobic Surface Modification of Silica-loaded Cotton.....	101
5.3.5. Batch Oil-water Separation.....	102
5.3.6. Continuous Oil-water Separation.....	102
5.3. Results and Discussions	103
5.3.1. Synthesis of Modified Cotton	103
5.3.2. Morphology and the Wettability of Prepared Cotton Wool	105
5.3.3. Chemical Properties of Cotton.....	107
5.3.4. Durability Test of Modified Cotton	110
5.3.5. Batch Oil-water Separation.....	111

5.3.6. Proof of Concept for Continuous Oil-water Separation	118
5.4. Conclusions	122
References	122
Chapter 6. Simple One-pot Fabrication of Durable Superhydrophobic Cotton Wool Using ODTMS Modified Silica-sol for Oil-water Separation	125
Abstract	125
6.1. Introduction	125
6.2. Materials and Methods	128
6.2.1. Cotton Pre-treatment.....	128
6.2.2. Synthesis of Superhydrophobic Cotton	128
6.2.3. Characterisation	128
6.3. Results and Discussions	129
6.3.1. Synthesis of Modified Cotton	129
6.3.2. Morphology and Wettability of Cotton.....	130
6.3.3. Chemical Properties of Cotton.....	132
6.3.4. Thermal Properties of Cotton	134
6.3.5. Durability Test of Modified Cotton	136
6.3.6. Oil-water Separation	137
6.4. Conclusions	140
References	141
Chapter 7. Synthesis of Superhydrophilic Cellulose Materials to Remove Oil from Oil-in-water Emulsions Before Disposal of Wastewaters to Sewers.....	145
Abstract	145
7.1. Introduction	146
7.2. Materials and Methods	147
7.2.1. Materials	147
7.2.2. Synthesis of Superhydrophilic Materials.....	148
7.2.3. Material Characterisation.....	148
7.2.4. Preparation of Emulsions.....	148
7.2.5. Emulsion Separation Experiment	149

7.3. Results and Discussions	149
7.3.1. Preparation of Superwetting and Superoleophobic Materials	149
7.3.2. Morphology of Cotton and Tissue paper	150
7.3.3. Surface Chemistry Analysis and Thermal Properties	151
7.3.4. Separation of Surfactant-Stabilised Emulsion: Performance Evaluation of Modified Materials	156
7.3.5. Separation of Surfactant-Stabilised and Surfactant-Free Emulsions, and Reusability Studies	159
7.4. Conclusions	160
References	161
Chapter 8. Conclusions and Future Outlook	163
8.1. Conclusions	163
8.2. Outlook.....	164
Appendix	166
A.1. Supplementary Information for Chapter 5.....	166
A.1.1. Calibrations Curves.....	166
A.1.2. SEM Images of A-C and N-C.....	166
A.1.3. Images of Beef Tallow Fats, Solid and Semi-solid, Before and After Filtration.....	167
A.2. Supplementary Information for Chapter 6.....	167
A.2.1. High Resolution C 1s Spectra of Pre-treated Cotton	167
A.2.2. Oil-water Separation	168
A.2.3. Synthesis of Modified Cotton	168
A.3. Permissions to Reproduce the copyright materials	170

List of Tables

Table 2.1 Elemental fatty acid composition in FOG deposits. ²	29
Table 2.2 Fatty acid content of common cooking oils and animal fats. ²	30
Table 2.3 Commonly used adsorption kinetic models. ⁴⁶	38
Table 2.4 Nonlinear column kinetic model equations. ⁴⁹	40
Table 4.1 Summary of the weight losses between 200-800 °C due to decomposition of functional groups.	92
Table 5.1 Elemental composition of cotton samples (atomic%).	109
Table 5.2 Values of the kinetic model parameters for the sorption of olive oil into modified cotton wool at room temperature.	116
Table 5.3 Values of the breakthrough model parameters for the continuous separation of olive oil from oil-water mixture.	120
Table 7.1 Binding energies of the detected elements of cotton and tissue paper.	153
Table 7.2 Binding energies of different chemical environments of each core level.	154
Table 7.3 Oil concentration in the filtrates.	159
Table A.1 Summary of all the copyright permissions obtained to reproduce materials from the original works.	170

List of Figures

Figure 2.1 Mean concentrations of fatty acids in the FOG deposits. Reproduced from ref. ⁵ with permission from Elsevier (© 2012 Elsevier Ltd.).....	29
Figure 2.2 Schematic illustration of the main events involved in MIC of concrete. ¹² Reproduced with permission. Copyright 2019, Elsevier.....	31
Figure 2.3 Proposed fatberg formation mechanism. Reproduced with permission from ref. ³ . Copyright 2013, Elsevier.	33
Figure 2.4 A typical retention-based GI for removing FOG from wastewater. ¹⁶ Reproduced with permission from Elsevier (© 2022 Elsevier Ltd.).....	34
Figure 2.5 Typical breakthrough curve from column study. Reproduced from ref. ⁴⁸ with permission from Elsevier (© 2021 Elsevier B.V.)	39
Figure 2.6 Different states of droplet on a solid surface. (a) Young model, (b) Wenzel model, and (c) Cassie–Baxter model.	43
Figure 2.7 Synthesis of activated carbon from biomass for dye removal from wastewater. Reproduced from ref. ⁴⁰ which is an open access paper with permission from American Chemical Society. Copyright 2020, American Chemical Society.	44
Figure 2.8 (a-l) Typical morphology of silica nanoparticles obtained from Stöber synthesis method, ⁷⁸ Reproduced from ref. ⁷⁸ with permission from Springer (© Springer Science+Business Media, LLC 2007). (m) Different particles morphologies and pore properties produced using modified Stöber synthesis method. ⁷⁵ Reproduced with permission from Elsevier (© 2014 Elsevier B.V.).....	46
Figure 2.9 Schematic illustration of the preparation of cotton using sol-gel method. Reproduced from ref. ¹¹⁸ which is an open access paper.	50
Figure 2.10 Schematic illustration of the dip-coating preparation and application of superhydrophobic sponge for oil-water separation and microplastic removal. Reproduced with	

permission from ref. ¹²¹ . Copyright 2023, Elsevier.....	52
Figure 2.11 Schematic showing fabrication of superhydrophobic ZnO coated meshes through spray coating method. Reproduced with permission from ref. ¹³⁰ . Copyright 2016, RSC publishing.	53
Figure 2.12 Oil absorption capacity of six types of oils, (b) separation efficiency of the modified melamine sponge with different types of oils, (c) stability test for superhydrophobic melamine sponge and (d) Reusability test of the modified melamine sponge, (e) morphology, wettability, and oil-water separation properties of the modified sponge. Reproduced with permission from ref. ¹⁵⁹ . Copyright 2021, Elsevier.	56
Figure 2.13 Illustration of the fabrication of superhydrophobic stainless steel mesh (c), Images showing oil-water separation (a) heavy oil-water and (b) light oil-water separation. Adapted from ref. ¹⁶¹ which is an open access paper.....	57
Figure 2.14 (a) Schematic diagram showing the preparation of superamphiphilic copper foam for selective separation of oil-water mixtures, (b, c) the oil-water separation property of the prepared copper foam, (d) the separation efficiency of the copper foam for various of oil-water mixtures. Adapted from ref. ¹⁷² with permission from Elsevier (© 2017 Elsevier B.V.)	59
Figure 2.15 (a) synthesis of pH-responsive cotton fabric, (b) mechanism of pH responsive cotton fabric, (c) changes WCA with pH (d) the WCA transition cycles of coated cotton fabric via pH treatment, (e) photographs showing removal of CHCl ₃ (dyed with Sudan III) and image of continuous separation of oil-water mixture, (f) removal process of water (dyed with methylene blue) sinking at the bottom of toluene and continuous separation of oil-water mixture, (g-h) images showing emulsion separation. Adapted from ref. ¹⁸³ with permission from Springer (© Springer-Verlag GmbH Germany, part of Springer Nature 2018).....	60
Figure 3.1 Chemical structure of the silica precursor and silanes used.	72
Figure 3.2 Typical free energy of adsorption for C ₆ -C ₁₀ n-alkane probes (n-alkane line) and free energy of adsorption of different polar probes.....	77

Figure 3.3 Abrasion testing set-up.	78
Figure 3.4 Calibration curves for different cooking oils in 5 mL hexane using UV-Vis spectrometer.	81
Figure 4.1 (a,b) SEM images of unmodified silica (a) N-SNPs, (b) A-SNPs. SEM images of one-pot modified silica particles (c) N-SP-C18, (d) A-SP-C18.....	89
Figure 4.2 WCA of the modified silica particles functionalised by both post-grafting and one-pot methods.	90
Figure 4.3 TGA curves of silica particles. (a) Silica particles from NaOH-catalysed synthesis, (b) silica particles from NH_3 -catalysed synthesis.	91
Figure 4.4 TGA curves of eggshells.	93
Figure 4.5 Performance testing of the powder adsorbents prepared. (a) maximum oil-sorption capacity of the powders at room temperature, (b) olive oil-water separation efficiency of the adsorbents at room temperature.	93
Figure 5.1 Schematic of the experimental set-up for the continuous flow separation.	102
Figure 5.2 Schematic illustration of the two-step preparation process of superhydrophobic cotton.	103
Figure 5.3 Overall mass gain of cotton wool during the two steps of preparation process.	104
Figure 5.4 SEM images of (a) raw cotton, (b) pre-treated cotton, (c, d) A- C_{NH_2} cotton sample at low and high magnification, i.e. cotton loaded with silica nanoparticles using ammonia as a catalyst, (e, f) N- C_{NH_2} cotton sample at low and high magnification, from silica-sol using NaOH as a catalyst, (g, h) ODTMS modified A- C_{NH_2} and N- C_{NH_2} cotton samples.....	105
Figure 5.5 (a) WCA of modified cotton samples, (b-c) images showing the superhydrophobicity of cotton by interactions with water, (d-e) water sorption of unmodified and modified cotton samples, respectively.....	106
Figure 5.6 XPS survey of cotton samples, (a) raw and pre-treated cotton, (b) unmodified silica loaded cotton samples and (c) superhydrophobic cotton samples, (d) surface energy of the cotton	

samples at 30 °C.....	108
Figure 5.7 Durability studies of different superhydrophobic cotton samples.	110
Figure 5.8 (a) Sorption capacity of olive and salmon oils on different modified cotton samples, (b-d) images visualising oil removal from water surface.	112
Figure 5.9 Maximum sorption capacity and separation performance of A-C-C18 cotton in a batch system.....	114
Figure 5.10 (a) effects of contact time on sorption capacity of modified cotton, (b) effects on temperature, with no mixing, and mixing rate at room temperature on separation efficiency of modified cotton in a batch system.....	115
Figure 5.11 (a) Room temperature regeneration of oil-soaked cotton using different methods, (b) reusability study of modified cotton over 20 separation cycles.....	118
Figure 5.12 The images showing the continuous oil-water separation at different stages (a) preparation of high oil concentration feed mixture, (b) initial stage of separation where packed cotton started adsorbing oil, (c) later stage where over half of the packing height is used up. ...	119
Figure 5.13 (a) Breakthrough curves of oil in packed column for 10 and 20 g/L oil feed concentrations, (b) breakthrough curve experimental data fitted with Thomas model.....	120
Figure 5.14 Effects of feed oil-water mixture concentration (a) and feed flowrate (b) on the volume of water treated at bed saturation point and the achieved separation efficiency.....	121
Figure 6.1 Schematic illustration of the synthesis process of superhydrophobic cotton.	129
Figure 6.2 (a-d) SEM images of raw cotton, pre-treated cotton, superhydrophobic cotton before and after compressed air treatment, respectively. (e) and (f) water uptake of the cotton fibres and hydrophobic testing using blue dyed water.....	130
Figure 6.3 (a-b) FTIR spectra and XPS survey of cotton samples, respectively. High resolution spectra of C 1s core level of (c) pristine cotton, (d) modified cotton. (e) High resolution spectra of Si 2p of modified cotton. (f) Surface energy of cotton.	132
Figure 6.4 TGA and DTG curves of pristine, pre-treated, and modified cotton under (a, c) nitrogen	

and (b, d) air atmosphere.....	135
Figure 6.5 WCA of the modified cotton after (a) pH and chemical durability testing, (b) Laundering and abrasion testing.....	136
Figure 6.6 (a) Photographs of (a) olive oil separation from water surface and (b) olive oil-in-water emulsion separation. (b) maximum oil sorption of modified cotton in pure oils. (c) oil-water separation efficiencies of different cooking oils. (e) reusability of cotton sorbent for olive oil-water mixture separation over 20 test cycles.	138
Figure 7.1 Synthesis of superhydrophilic through dip coating method.	150
Figure 7.2 Chemical structure of the PEI and PVP polymers.....	150
Figure 7.3 SEM imaging of cotton and tissue paper. (a-b) Pristine cotton and tissue paper, (c-d) coated cotton at low and high magnification, respectively, (d-e) coated tissue paper at low and high magnification, respectively.	151
Figure 7.4 (a) XPS survey of uncoated and coated tissue paper and cotton wool. (b-e) High resolution analysis of the C 1s core level of (b,c) pristine cotton and tissue paper, respectively, (d,e) coated cotton and tissue paper, respectively. (f) Deconvoluted N 1s core level of coated cotton.	152
Figure 7.5 (a) TGA analysis and (b) surface energy of uncoated and coated tissue paper and cotton wool, respectively.	155
Figure 7.6 (a, b) Separation of surfactant-stabilised olive oil-in-water emulsion using different coated substrates using gravity assisted flow and applied pressure system, respectively. (c, d) Microscope images of the prepared emulsion and the filtrate after separation using coated cotton, respectively. The inserts show the photographs of the emulsion and the filtrate.	157
Figure 7.7 Schematic representation of oil-in-water emulsion separation.....	158
Figure 7.8 (a) Separation of surfactant-stabilised and surfactant-free oil-in-water emulsions made from different oils. (b) Recyclability test of the coated cotton using olive oil surfactant stabilised emulsion under gravity assisted.	159

Figure A.1 Calibrations curves (a) pump flowrate, (b-e) oil concentration calibration, beef (b), chicken (c), coconut (d) and salmon oil (e).....	166
Figure A.2 (a,b) SEM images showing low silica nanoparticle loading in N-C and A-C cotton samples, respectively.....	166
Figure A.3 (a, b) Images of beef tallow fat and congealed beef tallow fat- water mixtures, (c, d) clean water collected after filtration using raw cotton wool.	167
Figure A.4 C 1s spectra of pre-treated cotton.	167
Figure A.5 Less stable oil-in-water emulsion separation.	168
Figure A.6 (a) Effects of ODTMS concentration on hydrophobicity of cotton. (b, c) wettability of modified cotton.	168

Chapter 1. Introduction

1.1. Background and Motivation

As industrialisation intensifies, the issue of oily wastewater and its appropriate disposal has become paramount for sustainable environmental management. Untreated oily wastewater poses grave threats to aquatic ecosystems, manifesting in the disruption of marine life, the degradation of water quality, and contamination of the food chain.¹⁻³ Moreover, the presence of oil in aquatic environments significantly jeopardises human health, raising the potential for adverse health impacts from consuming tainted seafood or exposure to polluted water.⁴ Notably, a significant portion of this oily wastewater comes from food processing plants, domestic households, and food service establishments.² These sources often exhibit high concentrations of fats, oils, and greases (FOGs) and without proper management, FOGs can accumulate over time within sewer pipelines and form solid deposits.⁵ Often, when FOGs enter sewer systems, they combine with non-biodegradable materials like sanitary products and solidify into large masses commonly known as fatbergs.⁶ This frequently leads to a restricted flow of wastewater and, in some cases, blockages within the sewerage system, resulting in sanitary sewer overflows (SSOs). According to a 2004 EPA report, 50% of SSO incidents in the U.S. stem from sewer blockages, with approximately half being attributable to FOG deposits.⁷ In the UK alone, it's estimated that fatbergs, account for 50-75% of all sewer blockage incidents.⁶ Furthermore, UK water companies spend between £15-£50 million annually in FOG removal by water jetting or manual methods.^{6,8} These figures underscore the pressing nature of the challenges arising from unmanaged FOGs.

In 2017, a massive fatberg was discovered in east London, Whitechapel, by Thames Water which according to the British Broadcasting Corporation (BBC) news weighed 130 tonnes.^{9,10} Previously, 10 tonnes and 15 tonnes of fatbergs were also discovered in London in 2015 and 2013, respectively.⁶ These fatbergs present a potential fuel source as they can, for example, be converted to biodiesel.⁶ However, there are challenges in this process like the energy needed for liquifying

the FOGs and separation of the solid components. Therefore, FOG recovery at the wastewater source points not only help with prevention of fatbergs in the sewers, but also help provide less contaminated FOG feedstock for biodiesel production.

Adopting the waste hierarchy, it will be difficult to eliminate the FOGs from the diet.⁶ Therefore, the 3 R's (Reduce, Reuse and Recycle) can be utilised. However, due to population growth and different diet habits, it will be difficult to reduce FOG consumption. The Food and Agriculture Organisation (FAO) in 2016 predicted a rise in global fats and oils production of about 5% and consumption of 3% for the years 2016 and 2017.^{8,11} Furthermore, FOG consumption per capita in most developed countries is estimated to be over 50 kg/a compared to developing countries which only consumes 20 kg/a.¹² Due to increased urbanisation, most people tend to move towards the western diet which leads to high consumption of fats and oils, consequently, resulting in the rise of FOG deposits.¹³ Furthermore, the reuse of FOGs e.g. reusing deep fry oils in restaurants poses health problems to the public.^{14,15} Thus, only the recycle of the FOGs to be used as fuel feedstocks offer the best sustainable FOG management practice.¹⁶

FOG-rich wastewater, due to their high biological oxygen demand (BOD), not only affect the sewer systems but also affect the performance of wastewater treatment plants and increase the plants' maintenance costs.¹⁷ Therefore, appropriate FOG management practice is crucial. The most common and easy way to reduce FOG deposits is through public awareness campaigns.⁶ These involve educational initiatives that promote better practices which, in turn, reduce the amount of fats and oils being disposed into the drains. However, these practices are not always effective because there are no incentives or policies to push people to adopt them. Therefore, it is best to have other measures in place. One such measure is the use of grease traps/interceptors (GIs), mostly in food service establishments, to reduce FOGs going down into the sewer pipes.^{6,17,18} Additionally, biological additives (e.g. enzymes or microbiological cultures) could also be used in the sewers to promote biodegradation of FOGs.⁷ Despite all these measures in place, problem of fatbergs in urban

areas is still prevailing. As such it is important to develop new technologies to combat the problem of FOGs and/or fatbergs.

Oil-water separation stands as a well-established research field, witnessing a growing body of research focused on the development of eco-friendly and sustainable materials for oil-water separation applications. While traditional grease GIs, relying on physical oil-water separation technique, may fall short in addressing FOG deposit issues, the utilisation of sorption/filtration methods presents a more effective solution. Many oil sorbents and filter materials have demonstrated outstanding performance, achieving oil-water separation efficiencies exceeding 90%.^{19,20} The simplicity, cost-effectiveness, and high efficacy of oil-water separation through sorption and filtration processes make them the superior alternative to existing FOG management techniques. Moreover, these processes exhibit versatility, being applicable to diverse types of oily wastewater, and they are easily scalable to accommodate varying levels of wastewater production. Therefore, their exploration as a solution for preventing FOG deposits is crucial, especially considering the absence of prior research in this particular domain.

1.2. Project Objectives

This research aims to investigate the implementation of sorption and filtration oil-water separation techniques as a proactive measure for recovering FOGs from wastewater before its discharge into sewer lines. The project encompasses the synthesis of sorbents/filters and their subsequent testing to evaluate their performance in oil-water separation. This includes the assessment of their effectiveness in separating solid fats and congealed fats from water.

In this study, silica sol-gel and dip-coating methods were employed to synthesise sorbents and filters for oil-water separation. Cotton wool was used as the main substrate; however, other cellulosic materials were explored in the emulsion separation work. The durability of the prepared materials under different working environments was investigated. Additionally, their performance in oil-water separation under different process parameters, including variations in the nature of cooking oils, was examined.

The specific project objectives are presented below:

- To synthesise and characterise sorbents with both superoleophilic and superhydrophobic surface properties for removal of oils and congealed fats from immiscible oil/fats-water mixtures.
- To determine the oil sorption capacity of the synthesised sorbents using different cooking oils and fats.
- To synthesise and characterise superhydrophilic/superoleophobic filter materials for separation of oils from oil-in-water emulsions.
- To evaluate separation performance of the prepared sorbents and filters under different process conditions for both batch and flow system set-up.

1.3. Thesis Structure

A total of 8 chapters, including the introduction, are presented in this thesis. Chapter 1 covers the background and the objectives of the research. Chapter 2 presents extensive review of the literature on the formation process of the fatbergs, current solutions and their limitations, application of superhydrophobic and superhydrophilic materials for oil-water separation. Chapter 3 outlines the research methodology, encompassing the experimental method and characterisation techniques employed in this study. Chapter 4 explores the initial investigations conducted with oleophilic silica nanoparticles and eggshell powders. It sheds light on various research challenges encountered when applying these powders to oil-water separation. Chapter 5 details the two-step synthesis process of superhydrophobic and superoleophilic cotton wool and its application for oil-water separation. The chapter provides insights into the morphology, chemical durability, and separation performance of the prepared cotton. Moving to Chapter 6, a quick one-pot synthesis method of superhydrophobic cotton is explored, and the separation performance of the sorbent is tested. Chapter 7 investigates the separation of oils from oil-in-water emulsion - a potential route by which FOGs enter the sewers. This exploration involves filtration technique using dip-coated

cotton wool and other cellulosic materials. Finally, Chapter 8 provides overall conclusions for the entire thesis and suggests recommendations for future work based on the current research.

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Chapter 2. Scientific Background and Literature Review

2.1. The Origins of Fatbergs and Their Formation Mechanisms

Fatbergs are large masses that form in sewer systems from the accumulation of fats, oils, and grease, combined with non-biodegradable materials such as wet wipes, diapers, sanitary products, and food debris.¹ These substances congeal and coalesce within sewage systems, particularly in sewer pipes and drains, where they can grow to massive sizes. The term "fatberg" is a combination of "fat" and "iceberg," emphasising their size and composition. In order to address the fatberg issue effectively, it is crucial to comprehend their formation process. Research, including studies by Keener et al.² and He et al.³, among others, indicates that fatbergs primarily consist of calcium salts of fatty acids formed through saponification reactions within sewer systems.

In 2018, the Water Science Institute at the University of Cranfield conducted an autopsy on a fatberg to identify its constituents.⁴ The analysis involved heating samples in a furnace up to 550 °C, which converted most of the solid components to ash. The oil was then extracted from the resulting product. The autopsy revealed that approximately 60% of the fatberg consisted of fats, predominantly composed of palmitic acid and oleic acid, with proportions of 53% and 18% respectively. Additionally, the samples were found to have higher concentrations of calcium metal ions compared to other metals such as magnesium, sodium, and aluminium. The findings from the CWSI study align with those of Keener et al.² and Williams et al.⁵, who also employed a similar analysis method. These studies extracted oil from fat, converting it to methyl and ethyl fatty acid esters using strong acids and methanol/ethanol, and then performed profiling analysis using Gas Chromatography with Flame Ionisation Detection (GC-FID). Table 2.1 and Figure 2.1 display the results of these studies. Calcium ion concentrations reported by Keener et al., Williams et al., and CWSI were 9100 ppm, 10 940 ppm, and 785 ppm respectively, markedly higher than concentrations typically found in hard water.

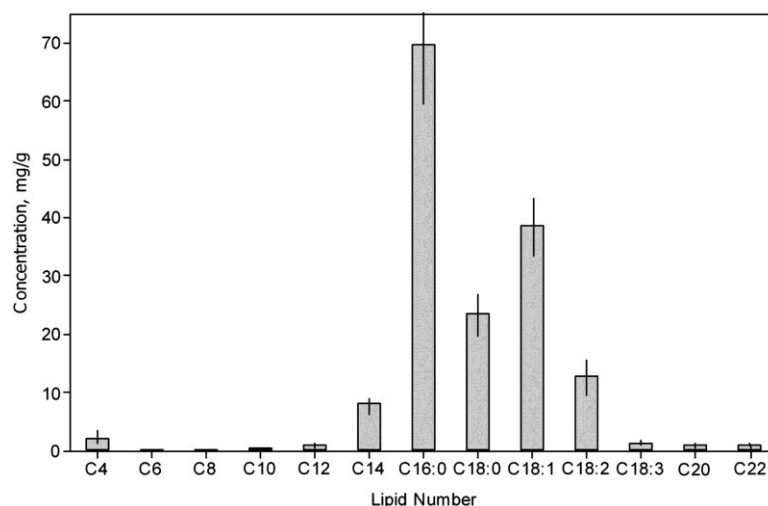


Figure 2.1 Mean concentrations of fatty acids in the FOG deposits. Reproduced from ref.⁵ with permission from Elsevier (© 2012 Elsevier Ltd.)

Table 2.1 Elemental fatty acid composition in FOG deposits.²

Sample	Saturated	Primary	Unsaturated	Primary
#	fat (%)	saturated fat	fat (%)	unsaturated fat
1	40.18	Palmitic	38.35	Oleic
2	87.07	Palmitic	8.33	Oleic
3	58.36	Palmitic	27.93	Oleic
4	69.97	Palmitic	21.26	Oleic
5	73.20	Palmitic	18.73	Oleic
6	80.42	Palmitic	14.58	Oleic

2.1.1. Sources of Free Fatty Acids

As previously mentioned, fatbergs form due to the presence of calcium soaps of fatty acids in sewer systems, originating from FOGs. These FOGs predominantly come from residential sources, as oily water is poured down drains, or from residual oils in food service establishments (FSEs) and food processing industries, often due to inadequate grease traps. A significant portion of the oils and fats entering drains from FSEs contains high levels of free fatty acids, a by-product of oil undergoing thermal hydrolysis during deep-frying.⁶ Some cooking oils used in the FSEs already have a significant portion of the free fatty acids. Certain food industries produce FOGs rich

in glycerides, abundant lipids found in many dietary fats and oils.⁷ However, when any oils and fats find their way into sewers, they are partially broken down by fungi and bacteria or undergo alkali-driven hydrolysis in sewage water to free fatty acids.⁸ Despite palmitic acid being identified as the primary fatty acid in fatbergs by several researchers, this does not align with the fatty acid profiles of commonly used cooking oils and animal fats, as shown in Table 2.2.

Contrary to expectations, oleic acid is found to be highly abundant in cooking oils and animal fats, suggesting a shift in fatty acid profiles within sewers. He and Yan demonstrated in their study that microbial activity in grease interceptors leads to the biodegradation of fats and oils into long-chain fatty acids.⁹

Table 2.2 Fatty acid content of common cooking oils and animal fats.²

Lipid type	Saturated fat (%)	Primary unsaturated fat	Unsaturated fat (%)	Primary unsaturated fat	Poly-unsaturated fat (%)	Primary poly-unsaturated fat
Cooking oils						
Canola	7.3	Palmitic	62.9	Oleic	30.5	Linoleic
Corn	13.6	Palmitic	25.6	Oleic	60.8	Linoleic
Olive	12.1	Palmitic	80.9	Oleic	7	Linoleic
Palm	49.4	Palmitic	39.5	Oleic	11.1	Linoleic
Peanut	19.4	Palmitic	48.5	Oleic	32	Linoleic
Soybean	15.4	Palmitic	23.3	Oleic	61.3	Linoleic
Animal fats						
Chicken	33	Palmitic	45.2	Oleic	21.4	Linoleic
Lard(pig)	41.8	Palmitic	47.9	Oleic	9.9	Linoleic
Tallow(beef)	47.9	Palmitic	47.4	Oleic	3.3	Linoleic

They also noted a significant presence of saturated fatty acids in the effluent, possibly resulting from the anaerobic degradation of long-chain unsaturated fatty acids into saturated ones. This

finding is supported by Pereira et al.¹⁰, who established that palmitic acid (C16:0) is typically abundant among other intermediates (C10:0 – C18:0) of anaerobic degradation of oleic acid via β -oxidation. Furthermore, the higher palmitic acid content in FOG deposits (as indicated in Table 2.1) compared to cooking oils and animal fats underscores that FOG deposits accumulate over time in sewers.

2.1.2. Calcium Ions

High concentrations of calcium metal ions have been discovered in FOG deposits, prompting speculation about their origin from water hardness.⁵ However, the reported levels of these ions far exceed typical water hardness levels, suggesting an additional source beyond food and water hardness. One possible contributor is the release of calcium ions from corroded concrete walls. Concrete corrosion has long plagued sewer systems, a concern documented as far back as Hammerton's 1944 study.³ Further research indicates that microbial activity within sewers can exacerbate concrete corrosion.^{11,12} This process involves the production of hydrogen sulphide gas (H_2S) by sulphate-reducing bacteria in the biofilm.

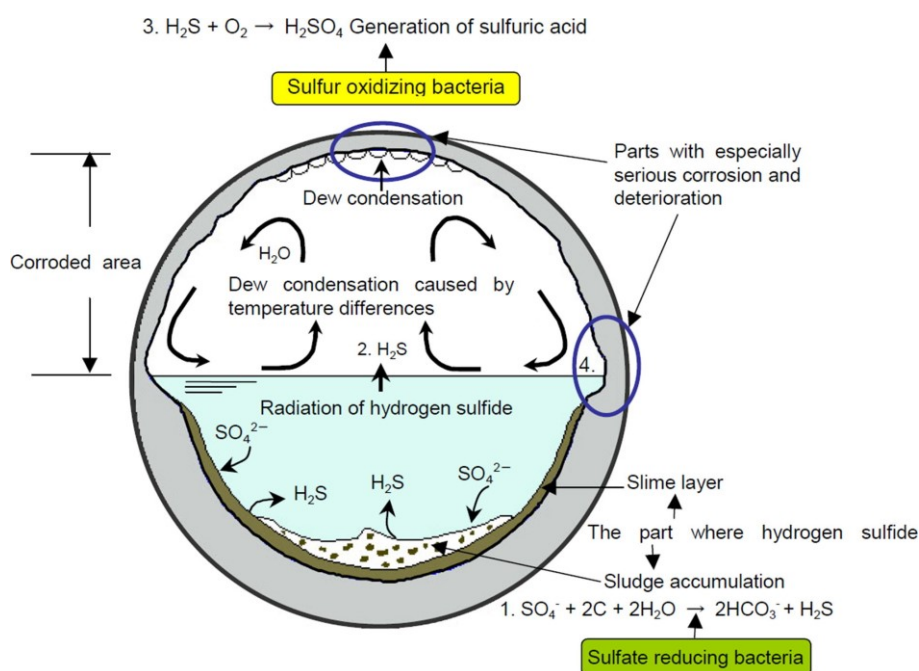


Figure 2.2 Schematic illustration of the main events involved in MIC of concrete.¹² Reproduced with permission. Copyright 2019, Elsevier.

Subsequently, H_2S is converted to sulphuric acid by sulphate-oxidising bacteria in the sewer atmosphere. The resulting sulphuric acid then reacts with concrete, liberating calcium ions. Figure 2.2 provides an overview of the key events contributing to microbially induced corrosion (MIC) of concrete.

2.1.3. Sewer Reaction Conditions

Recent research has elucidated that saponification reaction plays a pivotal role in FOG deposit formation. While industries typically induce saponification at high temperatures,¹³ sewer environments operate at much lower temperatures. The alkaline nature of sewers, with pH levels ranging from 7 to 9 due to the presence of alkaline detergents in sewage water, is believed to facilitate the saponification of fatty acids.¹³ He et al.³ demonstrated that saponification indeed occurs through alkali hydrolysis of fatty acids. The pH of the sewer also influences the solubility of calcium ion sources. Additionally, the aggregation of excess calcium ions and unreacted free fatty acids contributes to fatberg formation.³ According to the DLVO theory, unreacted fatty acids and calcium ions diffuse toward saponified fatty acids, which act as a core attached to sewer walls.¹⁴ Moreover, the rate of saponification is heightened at interfaces such as the FOG-water interface or FOG-concrete interface, implicating sewer flow patterns in FOG deposition. Lower flow rates in sewers result in extended contact times and increased aggregation.¹⁴ Considering the myriad factors affecting FOG deposits in sewers, He et al.³ proposed a mechanism for FOG deposit formation, depicted in Figure 2.3. Iasmin et al.⁸ carried out a study to investigate the effects FOG types and calcium sources on FOG deposition kinetics. The study utilised different sources of FOG (canola oil and beef tallow) and different calcium sources (calcium chloride simulating wastewater hardness and calcium sulphate simulating the calcium from concrete corrosion). The results showed that the source of both FOGs and calcium ions have a significant impact on the FOG deposition kinetics. Large quantities of saponified solids were observed with calcium sulphate and canola oil.

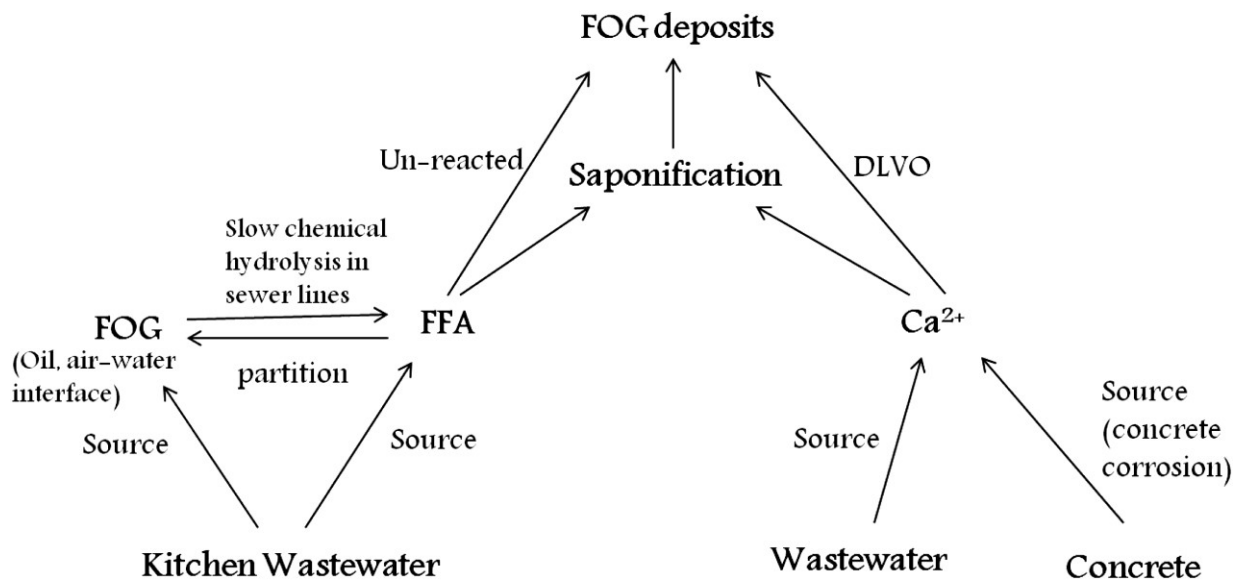


Figure 2.3 Proposed fatberg formation mechanism. Reproduced with permission from ref.³. Copyright 2013, Elsevier.

2.2. Current Methods of Mitigating FOG Deposits

When addressing the issue of fatbergs in sewers, there are two approaches to managing FOG deposits: addressing them at the source points where FOGs are produced and managing them within the sewer system itself.

2.2.1. Control at the Source Point

Examining the proposed FOG deposit mechanism (Figure 2.3), one effective control measure involves preventing FOGs and free fatty acids from entering sewers. Various proactive solutions exist to mitigate the entry of FOGs into sewer lines. One such solution is to raise public awareness about the detrimental effects of disposing FOGs and used cooking oils into drains.¹⁵ However, influencing human behaviour is complex and subjective, as success depends on individuals and this lacks enforcement by policies.¹⁵ Recently, due to advancements in the circular economy and sustainability initiatives, there's been a shift towards utilising used cooking oils for biodiesel production. This creates an incentive, particularly for FSEs, to participate in sustainable practices.

Another efficient proactive method of FOG management involves installing grease interceptors (GIs) to extract FOGs from domestic and food industry wastewater before disposal.¹⁶ GIs physically segregate FOGs from water based on density differences, allowing FOGs to

accumulate at the surface and food debris to settle at the bottom (Figure 2.4). GIs can be situated either below sinks (flow-based grease interceptors/FGI) or outdoors in the ground (retention-based grease interceptors/RGI). Clarified water is then discharged into the sanitary sewer system, while FOGs are extracted and collected by trucks. Regular maintenance and emptying of GIs are crucial for their efficiency, as operational factors such as inflow rate, suspended solids, biological/chemical oxygen demands, pH, and FOG concentrations fluctuate throughout the day, affecting Hydraulic Retention Time (HRT).¹⁷

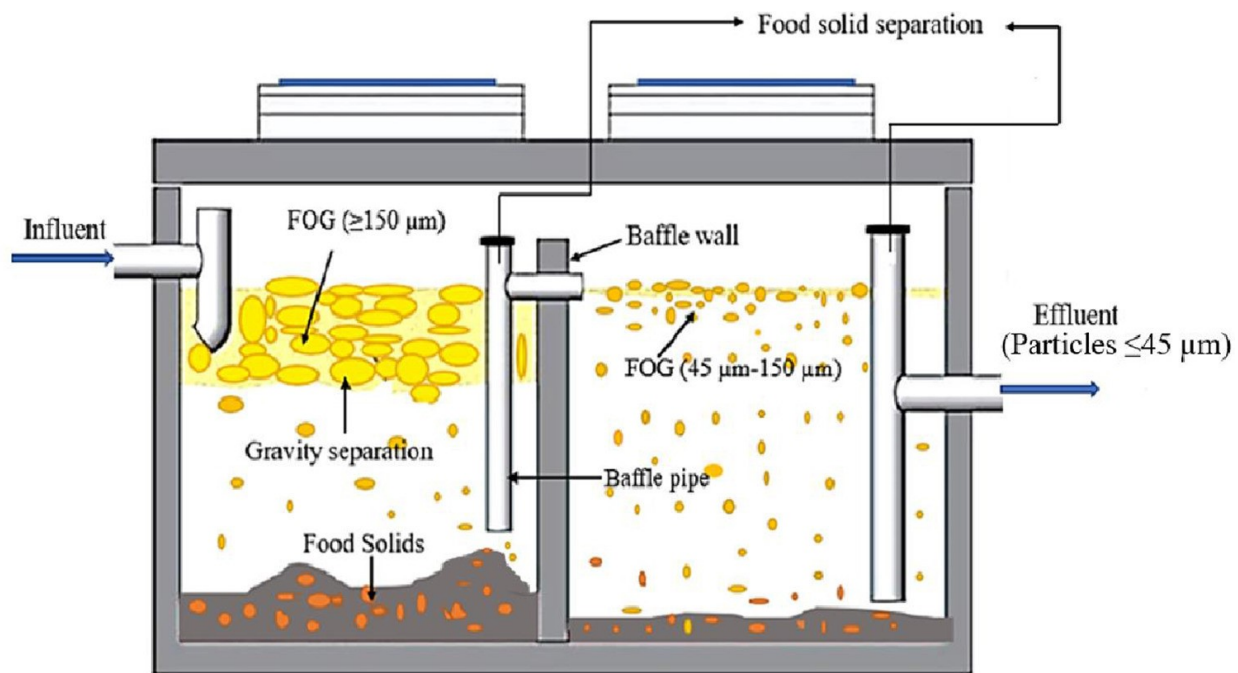


Figure 2.4 A typical retention-based GI for removing FOG from wastewater.¹⁶ Reproduced with permission from Elsevier (© 2022 Elsevier Ltd.).

Bioaugmentation presents another solution studied for FOG removal before wastewater disposal into sewers. Bioaugmentation involves enriching microbial populations in a specific environment to enhance targeted biological activities. In the context of FOG removal, this means introducing specialised microbial cultures into wastewater to improve degradation of FOGs. Studies by Brooksbank et al.¹⁸ demonstrated a significant enhancement of fats and oils degradation, up to 62%, after a 28-day incubation period.

Additionally, Tang et al.¹⁹ utilised Bio-Amp, a blend of aerobic and anaerobic bacteria, to degrade FOGs in GIs, resulting in reductions of 39% in chemical oxygen demand (COD) and 59% in total

fatty acids, leading to a subsequent 40% decrease in FOG deposits.

2.2.2. Control in the Sewers

Once FOGs have entered the sewer lines, several preventative measures have been studied to impede the formation of FOG deposits. Examining the proposed fatberg formation mechanism (Figure 2.3), it's evident that inhibiting the sources of calcium ions, free fatty acids, and saponification reactions is crucial to preventing FOG deposits. Additionally, bioaugmentation can be employed within sewers as well to remove FOG deposits and free fatty acids.^{14,20} Methods to prevent calcium ion sources include implementing concrete corrosion control techniques, such as applying corrosion-resistant and antimicrobial-coating layers to the inner surfaces of pipes.^{21,22} Another approach to control corrosion involves reducing hydrogen sulfide (H₂S) buildup in sewers through chemical dosing.²³ For example, magnesium hydroxide and sodium hydroxide have been utilised to neutralise H₂S in the liquid phase.²⁴ Once fatbergs have formed, measures are implemented to prevent blockages and mitigate the aftermath of fatbergs in sewers. Typically, manual removal of fatbergs is employed, which entails water jetting to break down fatbergs into smaller, more manageable sizes.⁵ Despite these efforts, fatberg-related issues persist as an ongoing challenge.

2.3. Limitations of the Current Solutions

Traditional FOG mitigation techniques come with inherent limitations and challenges, revealing a complex landscape of considerations. Mechanical strategies, such as GIs, are theoretically effective but necessitate regular maintenance and cleaning to prevent blockages and ensure optimal performance. The accumulation of FOG in these GIs can result in foul odours, reduced efficiency, and potential overflow issues if not managed meticulously. Despite these efforts, FOGs still find their way into sewers due to the relatively low efficiency of these methods. For example, research by Gallimore et al.²⁵ demonstrated that RGIs removed 80% of FOGs, FGIs achieved less than 50% removal efficiency under the tested conditions. Furthermore, the study

highlighted a significant decrease in the efficiency of GIs as temperatures and emulsion strength increased. Introducing chemical additives raises concerns about the environmental impact of these substances and the addition of extra chemicals into the wastewater stream, necessitating careful dosing and potential post-treatment. Biological methods, while promising, can be sensitive to environmental conditions such as temperature, pH levels, and nutrient availability, which may affect their effectiveness.

2.4. Utilisation of FOGs in Biodiesel Production

Biodiesel production represents a sustainable alternative to conventional fossil fuels, offering a renewable and eco-friendly source of energy.^{26,27} Typically, the production process involves converting vegetable oils, animal fats, or recycled cooking oils into biodiesel through chemical reactions such as transesterification, pyrolysis, and microemulsification.²⁶ Trebalsi et al.²⁸ achieved an impressive 80 wt% bio-oil with a heating value of 8843 kg/Kcal from used cooking oil using pyrolysis at 800 °C in a fixed bed reactor. In a separate study, Bora et al.²⁹ successfully developed microemulsion-based biofuel using waste cooking oil with the addition of butanol or ethanol. Conventionally, transesterification is conducted using homogeneous base or acidic catalysts such as NaOH and H₂SO₄.³⁰ Dias et al.³¹ attained 97% and 92% pure biodiesel from the transesterification of unused cooking oils (sunflower and soybean oils) and used cooking oil of the same oils, respectively, utilising sodium hydroxide (NaOH) and potassium hydroxide (KOH) as catalysts. The biodiesel production process involves converting the triglycerides in the oils to fatty acid methyl ester (FAMEs) and glycerol.²⁶ Thus, this process necessitates feedstock with fewer free fatty acids that react with base catalysts to form fatty acid salts. However, used cooking oils, fats, and grease often have high levels of free fatty acids,³¹ hence requiring pre-treatment to reduce the free fatty acid content before transesterification. Recent advancements have led to breakthroughs in the use of heterogeneous catalysts (CaO, SrO, MgO, Zeolites, etc) that do not require pre-treatment and can convert fatty acids to FAMEs as well.³⁰ Consequently, FOGs have been successfully utilised as feedstock for biodiesel production.^{32–36} Therefore, this research not

only addresses the fatberg problem in sewers but will also provide a cost-effective and sustainable feedstock for biodiesel production, aligning with sustainability and circular economy objectives.

2.5. Adsorption and Filtration-based Separation

Adsorption is surface phenomena which involve the adhesion of molecules, ions or atoms from one phase (liquid or gas) to the surface of another phase (liquid or solid) resulting in an adsorbate film on the surface.³⁷ The ions, atoms or molecules that have been transported to the surface and the phase they are concentrated on are referred to as adsorbate and adsorbent, respectively. When conditions (temperature, pH, etc) in the carrier phase are changed, the adsorbed molecules can be released back from the surface to the carrier phase, this process is known as desorption. Adsorbates can interact with the adsorbent surface through physical forces like Van der Waals or the formation of chemical bonds such as ionic and covalent bonds.³⁸ The former is referred to as physisorption and the latter is chemisorption. The adsorption process is among the widely used processes in wastewater treatment owing to its low cost, high performance, and easy operational design.³⁹ Adsorption have been utilised in wastewater treatment for removal of different pollutants like toxic heavy metal ions, organic dyes, petroleum oils and other pollutants.^{40–}
⁴² Different adsorbents that have been utilised includes nanomaterials, activated carbon, natural materials, e.t.c.^{40,43–45}

2.5.1. Adsorption Kinetics

Kinetics are important to determine both the rate and the mechanism of adsorption. The adsorption kinetics is of paramount importance on treatment efficiency and process design. The table below lists some of the popular kinetic models used in adsorption studies.

Table 2.3 Commonly used adsorption kinetic models.⁴⁶

Kinetic Model	Description
Pseudo first order	The earliest model which assumes that the rate of adsorption is proportional to the number of unoccupied adsorption sites on the surface. The model is as follows: $\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (11)$ Upon integration it becomes: $q_t = q_e(1 - e^{-k_1 t}) \quad (12)$ where q_t is the amount adsorbed at contact time t, q_e is the amount adsorbed at equilibrium, and k_1 is the pseudo first-order rate constant.
Pseudo second order	This model describes the adsorption reaction rate which is dependent on energetically heterogeneous active sites on the adsorbent; it is often used to describe chemisorption. $\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (13)$ From integration, the following equation is obtained: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$ Where other terms have the same meaning as in pseudo first-order model and k_2 is the pseudo second-order rate constant.

2.5.2. Packed Bed Adsorption

Continuous processes are desired due to easy monitoring of process parameters through inline analysis, which leads to consistent product quality and reduction in downtime. Packed bed adsorbers are common in industries due to their ease of operation. The performance of packed bed

columns is studied using breakthrough curves, which are plots representing the change in adsorbate concentration at the effluent over time. Furthermore, the mechanisms of adsorption in these columns are dependent on factors like axial dispersion, film diffusion resistance, intraparticle diffusion resistance (both pore and surface diffusion) and sorption equilibrium with the packed sorbent.^{47,48} In packed bed, the column is saturated from the inlet overtime, the saturated zone progressively moves down the column to the exit. In the saturated zone, the sorbent and adsorbate are in equilibrium.

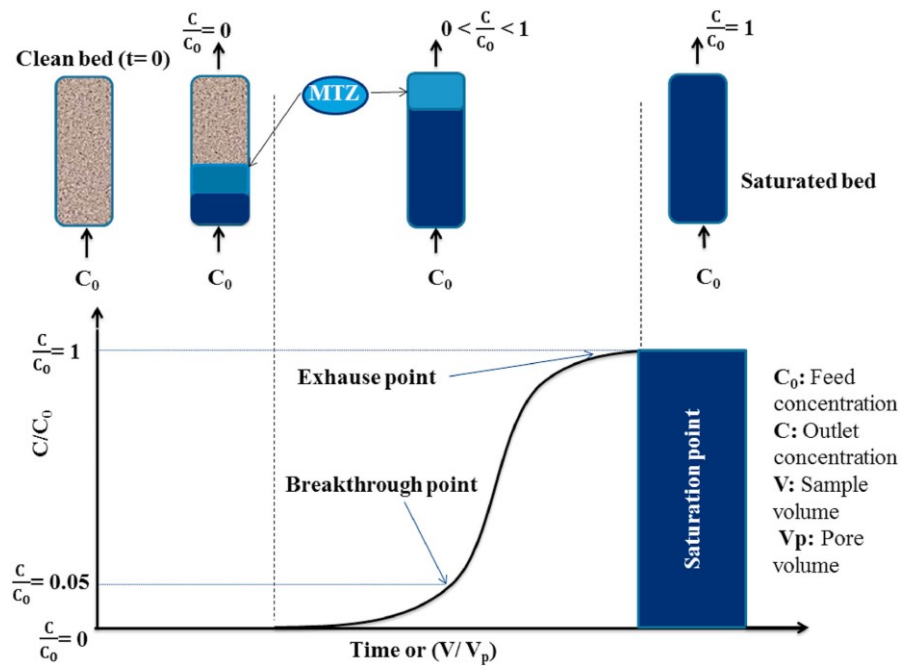


Figure 2.5 Typical breakthrough curve from column study. Reproduced from ref.⁴⁸ with permission from Elsevier (© 2021 Elsevier B.V.)

The region ahead of the saturated zone is referred to as the Mass Transfer Zone (MTZ). The typical breakthrough curve is shown in Figure 2.5. There are different models used to model the breakthrough behaviour of adsorbates and kinetics of adsorption (Table 2.4),⁴⁹ here only two models will be described. These models are the Thomas model and Yoon-Nelson model. The former ignores both the intraparticle diffusion resistance and external fluid film resistance, which means that the adsorption rate is controlled by the surface loading of adsorbate onto unused capacity of the adsorbent.⁵⁰ Yoon and Nelson's model is 'based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the

probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent.⁵⁰

Table 2.4 Nonlinear column kinetic model equations.⁴⁹

Model	Equation	Model Parameters
Thomas	$\frac{C_t}{C_0} = \frac{1}{1 + \exp \left[\frac{K_{TH}(q_e m - C_0 V)}{Q} \right]}$	q_e and K_{TH}
Adams-Bohart	$\frac{C_t}{C_0} = \exp \left(K_{AB} C_0 t - K_{AB} N_0 \frac{Z}{U_0} \right)$	K_{AB} and N_0
Wolborska	$\frac{C_t}{C_0} = \exp \left(\frac{\beta C_0 t}{N_0} - \frac{\beta Z}{U_0} \right)$	β and N_0
Yoon-Nelson	$\frac{C_t}{C_0} - C_t = \exp (K_{YN} t - K_{YN} \tau)$	K_{YN} and τ

Where q_e is the maximum column adsorption capacity, Q is the volumetric flowrate, m is the mass of adsorbent in the column, $V(Q \cdot t)$ is the effluent volume, N_0 is the saturation concentration, U_0 is the linear flowrate/velocity, Z is bed height, K_{AB} , K_{TH} , K_{YN} are kinetic constants and β is the external mass transfer coefficient.

2.5.3. Filtration Process

Filtration processes are fundamental in various industries, including water treatment, pharmaceuticals, food and beverage production, and chemical processing. The principle of filtration involves the separation of solid particles from a fluid (liquid or gas) by passing the mixture through a porous medium or filter media.⁵¹ For liquid-liquid filtration, membrane-based materials are often applied. The popular membrane filtration processes, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.⁵² It explains how membranes act as barriers, selectively allowing certain molecules or particles to pass through while retaining others based on their size, charge, or molecular weight. In the context of oil-water separation membranes/filters

have been applied for treatment.⁵³ However, most studies use chemistry-based filtration where the filter medium only allows one phase through and repels the other phase.⁵³

2.6. Sorption and Filtration in Oil-water Separation

Sorption processes have been studied for oil-water separation especially in the petroleum sector as a potential solution for oil spills in the oceans.^{54,55} No specific study was conducted to focus on the removal of FOGs using adsorption, however some of the studies on sorption-based oil-water separation have used cooking oils in their investigations.^{56–58} Filtration processes have shown to be effective as well for oil-water separation.⁵³ Mainly superhydrophobic materials are used for the oil-water separation studies because of their high selectivity towards oil.⁵⁹ The separation set-up when using these materials can also use filtration as a separation process.

2.6.1. Types of Oily Wastewater

2.6.1.1. Immiscible Oil-water Mixtures

An immiscible oil-water mixture refers to a combination of two liquids, oil and water, that do not dissolve or mix to form a homogeneous solution. Instead, they remain separate phases due to differences in their chemical properties. Oil is a nonpolar substance, composed primarily of hydrocarbons, while water is a polar molecule. Because of this polarity difference, oil and water do not readily mix. When these two liquids are combined, they form distinct layers, with oil floating on top of the water due to its lower density. In the case of heavier oils, the water phase tends to float above the oil phase when they are mixed. In the context of FOGs, all the edible oils and fats have lower density compared to water. These oil-water mixtures can easily be removed by superhydrophobic/superoleophilic sorbents or filters.⁵³

2.6.1.2. Oil-in-water Emulsions

Despite their immiscibility, oil and water can form emulsions under certain conditions. An emulsion is a stable mixture of two immiscible liquids, where one liquid is dispersed in the form of small droplets throughout the other liquid. For example, oil-in-water emulsions consist of tiny

oil droplets dispersed in a continuous phase of water, stabilised by surfactant molecules. The surfactants adsorb at the oil-water interface, forming a protective layer that prevents coalescence of the droplets.⁶⁰ Alternatively, stable emulsions can be produced through shear mixing or sonication, dispersing oil droplets into the water phase. Emulsions, particularly those with droplet sizes less than 20 μm , present challenges in separation processes due to their robust stability.

2.7. Superhydrophobic Materials

Superhydrophobic materials are surfaces or coatings that exhibit extreme water repellence. These materials have the ability to repel water to an extraordinary degree, causing water droplets to bead up and roll off the surface rather than wetting it.⁶¹ The term "superhydrophobic" comes from the combination of "super" (meaning extremely) and "hydrophobic" (meaning the fear or avoidance of water). The properties of superhydrophobic materials arise from their micro- or nano-structured surfaces, which feature a combination of low surface energy and intricate surface geometry.^{61,62} These structures create air pockets at the surface, minimising contact between water and the material. As a result, water droplets tend to form nearly perfect spheres and exhibit very high WCA with the surface, typically greater than 150° . Superhydrophobic materials are inspired by natural phenomena such as the lotus leaf which possesses micro- and nano-scale structures, combined with a wax-like coating, which give rise to its remarkable self-cleaning abilities and water-repellent surface.^{62,63} Researchers have sought to mimic these structures and properties in synthetic materials for various applications, including self-cleaning surfaces, anti-icing surfaces, oil-water separation, etc.^{62,64}

The wetting of surfaces refers to the ability of a liquid to spread across or adhere to the surface of a solid, rather than forming droplets or beads on the surface.⁶⁵ It is determined by the balance between adhesive forces, which pull the liquid molecules toward the surface of the solid, and cohesive forces, which hold the liquid molecules together. If adhesive forces prevail over cohesive forces, the liquid wets the surface. The extent of wetting is influenced by factors such as surface tension, surface energy, and the chemical properties of both the liquid and the solid. Typically,

wetting is assessed through the measurement of the contact angle between the liquid and the solid surface.⁶⁵

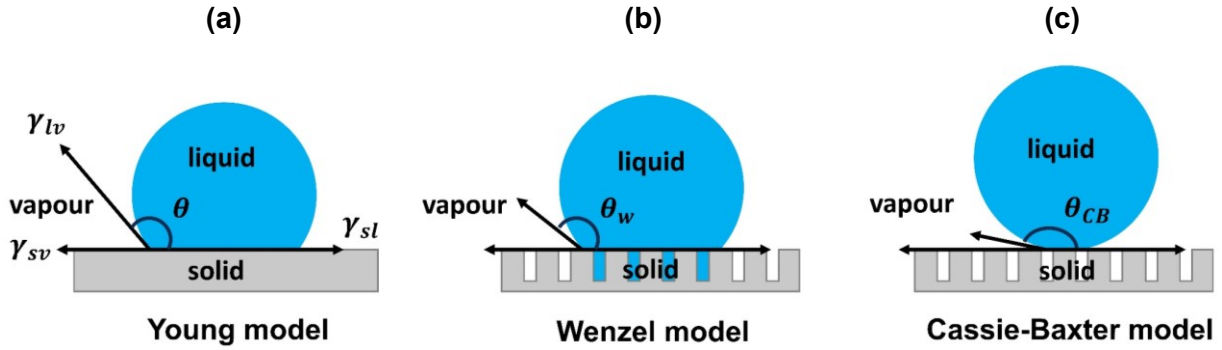


Figure 2.6 Different states of droplet on a solid surface. (a) Young model, (b) Wenzel model, and (c) Cassie–Baxter model.

Young's Equation

In 1805, Thomas Young⁶⁶ proposed a model to describe the wetting of an ideal smooth surface with water droplet using the surface force analysis.⁶⁷ Young's equation is given as:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (2.1)$$

where θ is the static liquid contact angle; γ_{sv} , γ_{sl} , and γ_{lv} represent surface tension of solid–vapour, solid–liquid, and liquid–vapour, respectively.

Wenzel Model

in 1936, Wenzel modified the Young's equation to account for the effect of surface roughness on the liquid's contact angle.⁶⁸ The roughness factor (r) was introduced as an effect. The Wenzel model is shown below.

$$\cos\theta_w = r \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} = r \cos\theta \quad (2.2)$$

Cassie–Baxter Model

Cassie–Baxter, in 1945, introduced a different model where liquid does not penetrate the grooves on rough surface and leaves the air gaps.⁶⁹ This model is often used for the porous and hydrophobic media.⁶⁷

$$\cos\theta_{CB} = f_{sl}\cos\theta_{sl} - f_{lv}\cos\theta_{lv} \quad (2.3)$$

where f_{sl} and f_{lv} are the fraction between the solid–liquid and liquid–air interface at the contacted area and air. θ_{CB} and θ_{lv} are the apparent contact angle of liquid droplet on rough surface under Cassie–Baxter state and the contact angle of liquid on ideal air surface ($\theta_{lv} = 180^\circ$), respectively. θ_{sl} is the apparent contact angle under Young’s state.

2.7.1. Synthesis of Superhydrophobic Powders and their Application in Oil-water Separation

Different techniques have been employed to synthesise different superhydrophobic powdered materials for their application in oil-water separation.

2.7.1.1. Activated Carbon

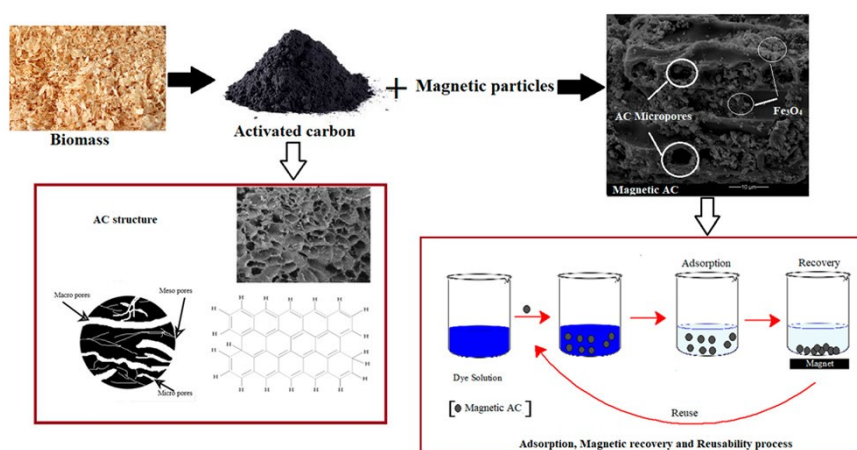


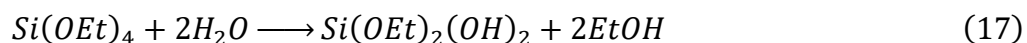
Figure 2.7 Synthesis of activated carbon from biomass for dye removal from wastewater. Reproduced from ref.⁴⁰ which is an open access paper with permission from American Chemical Society. Copyright 2020, American Chemical Society.

Activated carbon, also known as activated charcoal, is a form of carbon that has been processed to have a large surface area per unit volume.⁷⁰ This increased surface area is due to the presence of numerous small pores and cavities within the carbon structure.⁷¹ Activated carbon is produced from carbonaceous materials, such as wood, coconut shells, peat, coal, or lignite, through a process called activation after or before pyrolysis (Figure 2.7).^{71,72} Physical activation involves use of N_2 , CO_2 or high temperature steam to treat a carbonised material whereas chemical activation methods involve the use of dehydrating activating agents such as H_3PO_4 , KOH , $NaOH$, etc before pyrolysis.^{71,72} Different post modification techniques have been utilised to hydrophobise

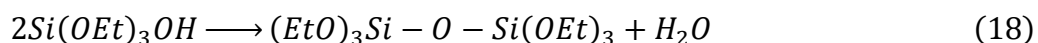
the activated carbon to form superhydrophobic surfaces. Sun et al.⁷³ used polydimethylsiloxane (PDMS) to modify the activated carbon to achieve WCA of 163.6°. Vapour chemical decomposition (VCD) is another method that is commonly used, Betar et al.⁴⁰ obtained WCA of 173° after chemical deposition of a bi-catalyst (Fe/Co) on a powder activated carbon.

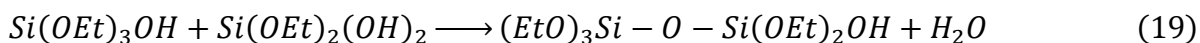
2.7.1.2. Silica Sorbents

Silica is a naturally occurring mineral in the earth's crust consisting of silicon and oxygen elements. It is also found as a major component of sand in many parts of the world. Naturally occurring silica is mostly found in crystalline form and rarely in the amorphous state.⁷⁴ On the other hand, synthetic forms of silica that exist mostly have the amorphous structure.⁷⁴ The types of amorphous silica include pyrogenic (fumed), silica gel and colloidal/precipitated silica. The common form of silica used in research is precipitated silica because of easier synthesis method. The simple sol-gel method commonly used is the Stöber synthesis method which involves the alkaline hydrolysis of silica precursor, mostly tetraorthosilicate (TEOS) in an alcohol solution.^{75,76} Additionally, it allows for the control of particle size over a range of 50-2000nm depending on reaction conditions.⁷⁶ The reaction pathway is described as a one-step process because both the hydrolysis and condensation occur consecutively in the same mixture. The reaction mixture is prepared by mixing TEOS with an ethanol-water mixture and finally adding ammonia as a catalyst to initiate the reaction.⁷⁶ Ethanol is used as a co-solvent to facilitate mixing of TEOS and water. The equations below show the reactions involved in silica particle formation from the hydrolysis of TEOS in ethanol.⁷⁷



The hydrolysis of TEOS produces ethanol/ and a mixture of ethoxysilanols which can then condense by loss of alcohol or water. Condensation results in the formation of a $\equiv Si-O-Si \equiv$ network as shown below:





The ageing of the reaction mixture promotes cross-linking through polycondensation of monomers and oligomers to form -Si-O-Si- network to grow existing small particles.

This approach is recognised for its ability to yield spherical, monodisperse silica nanoparticles (Figure 2.8a-l).⁷⁸ By incorporating surfactants or polymers as pore-directing agents, the method can be adapted to produce porous silica structures (Figure 2.8m).^{75,78} Additionally, silica particles can be derived from agricultural waste, offering a more environmentally sustainable alternative.⁷⁹

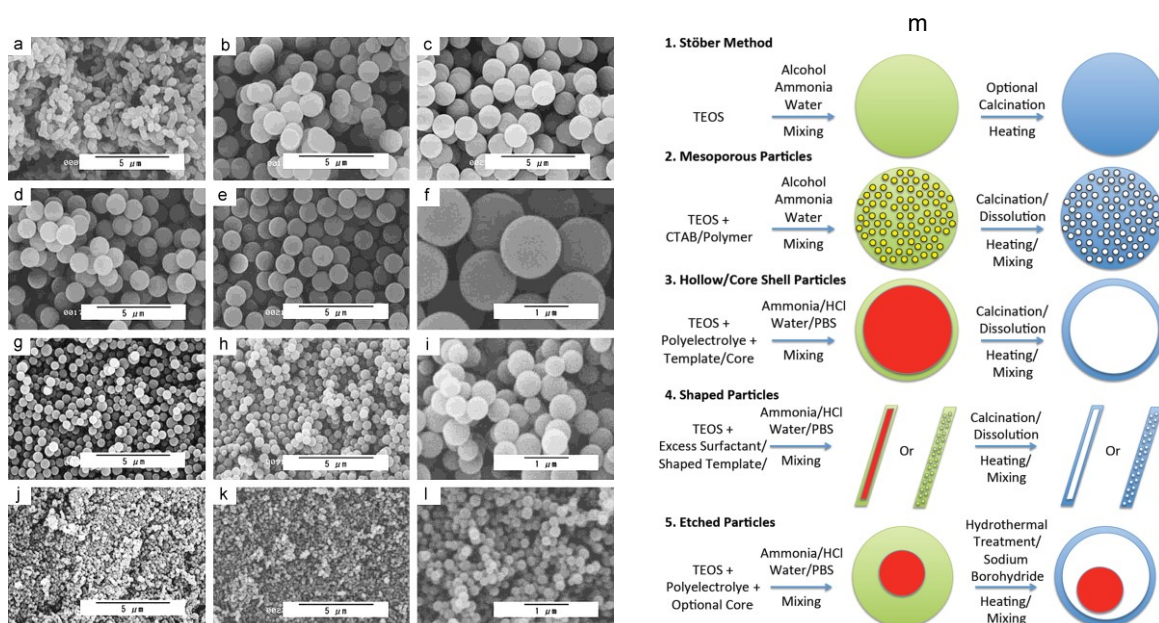


Figure 2.8 (a-l) Typical morphology of silica nanoparticles obtained from Stober synthesis method,⁷⁸ Reproduced from ref.⁷⁸ with permission from Springer (© Springer Science+Business Media, LLC 2007). (m) Different particles morphologies and pore properties produced using modified Stober synthesis method.⁷⁵ Reproduced with permission from Elsevier (© 2014 Elsevier B.V).

Due to the high concentration of silanol groups on the surface of silica particles, they can be easily modified to adjust their chemistry for specific applications.⁸⁰ Superhydrophobic silica nanoparticles have been successfully prepared using a post-grafting silanisation technique with hydrophobic silanes.⁸¹ For example, Chen et al.⁸² employed post-grafting with octyltrimethoxysilane (OTMS) to create superhydrophobic silica nanoparticles.

One-pot/co-condensation synthesis is another commonly used method for producing superhydrophobic silica nanoparticles.^{83–85} This technique involves both silica formation and functionalisation taking place in the same reaction mixture.⁸⁶ Typically, traditional silica synthesis

and surface modification processes are time-consuming, making co-condensation a time-saving alternative. Moreover, it allows for the incorporation of larger organic groups that may experience steric hindrance in post-grafting. However, with this method, achieving control over the final particle morphology and the distribution of functional groups on the surface can be challenging.⁸⁷ Stovpiaga et al.⁸⁸ synthesised superhydrophobic spherical silica particles (with a WCA of 155°) through base hydrolysis of TEOS and phenyltriethoxysilane (PTEOS) in the presence of cetyltrimethylammonium bromide. Their study demonstrated the efficacy of this prepared silica powder in adsorbing oil at the water surface. Similarly, Syed et al.⁸⁹ showed that hydrophobic nano-silica (Aerosil R812) is highly effective in treating water contaminated with gasoline and diesel, achieving over 97% separation efficiency.

2.7.1.3. Calcium Carbonate Sorbents

Calcium carbonate is a chemical compound represented by the formula CaCO_3 . It is commonly found in rocks, marine organism shells, eggshells and various mineral forms like calcite, aragonite, and vaterite.^{90–93} Widely utilised across industries, calcium carbonate finds applications in construction, pharmaceuticals, food and beverages, and cosmetics.⁹⁴ Although not inherently superhydrophobic, calcium carbonate can be tailored or combined with other substances to attain superhydrophobic properties. Arbatan et al.⁹⁵ demonstrated the modification of calcium carbonate using stearic acid and sodium hydroxide (NaOH) in water, proving effective in crude and diesel oil removal. Furthermore, Hu and Deng achieved superhydrophobic calcium carbonate by employing fatty acids (stearic and oleic acids) in both hexane and water, achieving advancing and receding WCAs exceeding 160°.⁹⁶ Mechanochemistry offers one of the simplest methods for hydrophobising calcium carbonate. This branch of chemistry explores chemical reactions induced by mechanical force, such as grinding, milling, or shearing, rather than relying solely on solvents or heat.⁹⁷ Its growing prominence stems from its potential for sustainable and efficient synthesis.

2.7.1.4. Other Powder Sorbents in Oil-water

Various powdered materials have been employed for oil-water separation. Okiel et al.⁹⁸

conducted extensive research on removing oil from oil-water emulsions using bentonite, powdered activated carbon, and deposited carbon. Bagasse, the fibrous residue obtained from sugar cane processing, has been carbonised and utilised in oil-spill treatment involving gas oil and Arabian crude oil.⁹⁹ Moreover, superhydrophobic and superoleophilic 5A zeolite was developed through surface modification with stearic acid, achieving a WCA of 156.2° and 98% kerosene removal from water.¹⁰⁰ Additionally, powdered sorbents such as chitosan and rubber powder have proven effective in removing residual oil from palm oil mill effluent.^{101,102}

2.7.2. Durability

The durability of adsorbents is a critical aspect that determines their effectiveness and practicality for various applications. Durability refers to the ability of an adsorbent to maintain its structural integrity, surface properties, and adsorption capacity over extended periods of use or under harsh operating conditions.¹⁰³ Factors affecting the durability of adsorbents include chemical stability, mechanical strength, resistance to fouling, regeneration capability, and long-term performance stability. Chemical stability is crucial to ensure that the adsorbent does not degrade or undergo undesirable chemical reactions when exposed to the target adsorbates or other environmental conditions. One common method frequently employed involves immersing the adsorbents in various organic chemical solvents, as well as solutions of different pH.¹⁰³ Mechanical strength is essential for withstanding handling, agitation, and pressure during adsorption processes without undergoing physical degradation or fragmentation. Typically, tape peeling or abrasion testing is utilised to evaluate the mechanical stability of the materials.¹⁰⁴ Resistance to fouling, such as by contaminants or impurities present in the feed stream, helps maintain the adsorption capacity and efficiency of the material over time.

2.7.3. Reusability

The reusability of adsorbents is paramount for economic and environmental sustainability across various industries. Extending the lifespan of adsorbent materials significantly reduce production costs associated with acquiring new materials. Additionally, reusing adsorbents

minimises waste generation and conserves valuable resources.¹⁰⁵ Regeneration processes, such as heating or chemical treatment, can restore the adsorbent's functionality, ensuring consistent performance over multiple cycles of use.^{106,107} Embracing the reuse of adsorbents not only promotes resource conservation and waste reduction but also aligns with broader sustainability goals, contributing to the circular economy and minimising environmental impact.

2.7.4. Large-scale Superhydrophobic Sorbents/Filters

Other than powders, other larger scale materials like foams, sponges, cotton wool, fabrics, etc are widely utilised and studied for oil-water separation.^{108,109} These materials offer enhanced surface areas, facilitating increased contact between the material and the oil-water mixture, thereby improving oil sorption and separation efficiency.¹⁰⁸ Additionally, they possess superior retention capacities, allowing them to hold larger volumes of oil, which is particularly beneficial for scenarios involving substantial oil contamination. Their ease of handling and adaptability to different setups make them preferable options, as they can be shaped or formed to suit specific separation requirements. Moreover, they are often reusable after oil extraction, reducing waste and operational costs compared to single-use powders. Their compatibility with mechanical systems further enhances their utility, enabling integration into automated or continuous separation processes. Overall, the choice of foams, sponges and other large-scale materials over powders depends on factors such as application requirements, material properties, and the need for efficiency and ease of handling. The common preparation methods of superhydrophobic surfaces on the large-scale materials include spray coating, dip coating, sol-gel method, etc. These methods work by modifying the surface chemistry and/or roughness of the materials used.

2.7.4.1.Sol-gel Method

The sol-gel method is a versatile wet chemical process used to produce solid nano-structured materials (usually metal oxide nanomaterials) from small molecules dissolved in a solution. Initially, a precursor solution is prepared by dissolving metal alkoxides or metal salts in water or alcohol solvent. The mixture undergoes hydrolysis and condensation reactions, which causes the

precursor molecules to link together, forming a three-dimensional network of small colloidal particles suspended in a liquid called a sol.¹¹⁰ The sol is then allowed to age or mature by gelling into wet-gels through continued polycondensation of the sol particles, leading to further cross-linking and densification of the material with expanded network of polymeric oxides interconnected by oxo-bridges.^{110–112} Subsequently, the solvent is removed from the particles through drying, resulting in the formation of a porous solid material called a xerogel or aerogels.^{113,114} The aging of the sol through precipitation results in uniform powders.¹¹³ Additional treatments such as calcination or further chemical modifications may be applied to enhance the properties of the final material. The sol-gel method offers precise control over the composition, structure, and properties of the resulting materials at the nanoscale, making it widely applicable in preparing superhydrophobic surfaces of sponges, cotton, etc. Silica and titanium nanoparticle sols are widely utilised in the preparation of superhydrophobic materials.¹¹⁵ For instance, Li et al.¹¹⁶ achieved superhydrophobic cotton fabrics through a one-pot sol-gel reaction using TEOS and hydroxyl-terminated polydimethylsiloxane (HPDMS), with ammonium polyphosphate acting as a coupling agent between the cotton fabrics and silica sol. This process resulted in a superhydrophobic fabric surface with a WCA exceeding 160°.

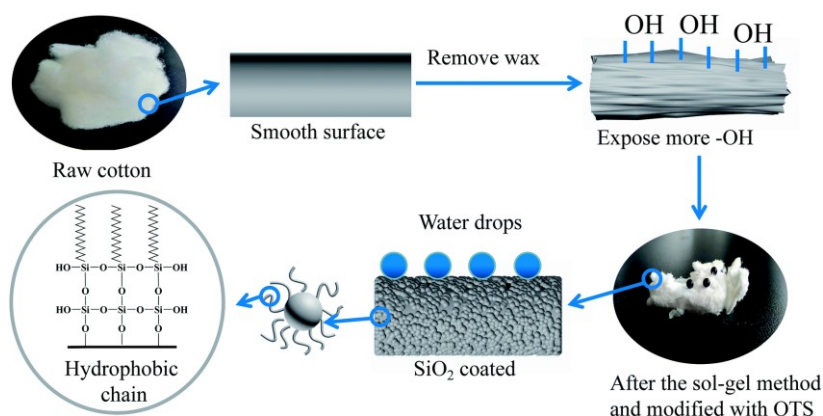


Figure 2.9 Schematic illustration of the preparation of cotton using sol-gel method. Reproduced from ref.¹¹⁸ which is an open access paper.

In an additional study, Shuai et al.¹¹⁷ developed a superhydrophobic polyurethane sponge using titanium oxide sol, followed by modification with poly(dimethylsiloxane) (PDMS). The prepared

sponge exhibited water repellence with a WCA of 154°. Furthermore, Lv et al.¹¹⁸ fabricated superhydrophobic cotton wool using a silica nanoparticle sol-gel method, followed by functionalisation with octadecyltrichlorosilane (Figure 2.9).

2.7.4.2. Coating Methods

Dip coating is a popular technique used to create thin coatings on substrates that impart superhydrophobic properties. This process involves immersing the substrate into a solution containing hydrophobic materials, such as fluorinated compounds or nanoparticles, followed by curing to enhance attachment.^{119,120} The success of dip coating for superhydrophobic surfaces depends on several factors, including the composition of the coating solution, the withdrawal speed, and the surface properties of the substrate.¹²¹ The goal is to create a rough or textured surface with low surface energy, which promotes the formation of air pockets when in contact with water, resulting in the superhydrophobic effect. Dip coating is favoured for creating superhydrophobic surfaces due to its simplicity, scalability, and versatility. Additionally, dip coating allows for precise control over coating thickness and morphology,^{122,123} enabling the fabrication of tailored superhydrophobic surfaces with desired properties. Gong et al.¹²⁴ employed dip coating to craft a superhydrophobic melamine sponge for oil-water separation. Their study utilised a superhydrophobic hyper-crosslinked microporous polymer (SHMP-1), with PDMS serving as a crosslinker to adhere SHMP-1 to the melamine sponge, resulting in a WCA of 156°. The chemical durability of the coated sponge was investigated by immersing it in solutions of varying pH levels (1-12), the results revealed that the polymer coating remained stable with WCAs consistently above 150° under all tested conditions.

Sutar et al.¹²⁵ developed a superhydrophobic stainless steel mesh for oil-water separation using a multilayer deposition dip-coating technique involving polystyrene and octadecyltrichlorosilane. The prepared stainless steel exhibited high superhydrophobicity, confirmed by a WCA of 157.5°, along with exceptional mechanical durability validated through adhesive tape tests, sandpaper abrasion tests, bending, twisting, and folding tests. In another study,

Yang et al.¹²⁶ developed superhydrophobic copper mesh (SHCM) (WCA~155°) for oil-water separation with stearic acid using one-step immersion ethanol solution. The study explored the durability and performance of SHCM under various environmental conditions, such as exposure to different pH values and high salinity environments. The SHCM maintained its superhydrophobicity when exposed to solutions with pH values ranging from 1 to 14, indicating resistance to corrosion from acidic or alkaline solutions.

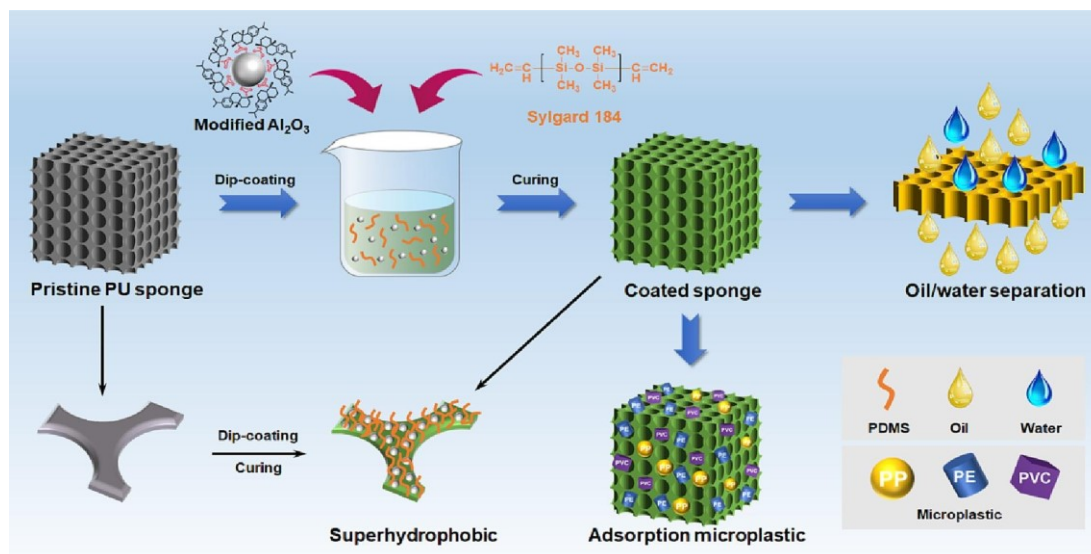


Figure 2.10 Schematic illustration of the dip-coating preparation and application of superhydrophobic sponge for oil-water separation and microplastic removal. Reproduced with permission from ref.¹²¹. Copyright 2023, Elsevier.

Additionally, it was found that immersion in a 3.5 wt% NaCl solution for seven days does not diminish its superhydrophobic properties. Even under the impact of high-water flow and abrasive conditions, the SHCM retains its effectiveness for oil-water separation. Unfortunately, continuous grinding with sandpaper led to loss of superhydrophobicity due to microstructure damage. Furthermore, Liu et al.¹²¹ also employed dip coating to produce a superhydrophobic sponge for oil-water separation and microplastic removal. Their method utilised PDMS and dehydroabietic acid modified hydrophobic Al₂O₃ nanoparticles (Figure 2.10).

Spray coating is another commonly employed method for preparing superhydrophobic surfaces,^{127–129} which entails applying a thin layer of material onto a surface using a spray gun or nozzle. It also involves preparing the surface by cleaning and sometimes priming it or pre-treating to ensure proper adhesion of the coating.¹³⁰ Using a spray gun or nozzle connected to a compressed

air system, the operator applies the coating material/solution evenly onto the surface, ensuring uniform coverage. After application, the coated surface undergoes a drying or curing process similar to dip coating. Li et al.¹³⁰ demonstrated fabrication of superhydrophobic stainless steel mesh using spray coating with stearic acid modified ZnO nanoparticles (Figure 2.11). The prepared mesh displayed a WCA of 154°. Additionally, the study manipulated water adhesion by altering the composition of the ZnO suspension, utilising both hydrophilic and hydrophobic ZnO nanoparticles.

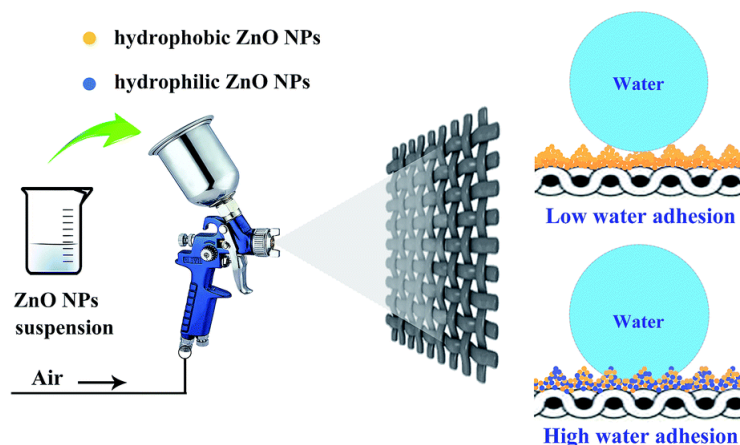


Figure 2.11 Schematic showing fabrication of superhydrophobic ZnO coated meshes through spray coating method. Reproduced with permission from ref.¹³⁰. Copyright 2016, RSC publishing.

In a separate study, Liu et al.¹³¹ described a simple fabrication of superhydrophobic cotton fabric by spray coating using silica@poly(dodecafluoroheptylmethacrylate) (SiO₂@PDFMA) nanocomposites and subsequent hot-pressing process. This process achieved superhydrophobicity with a WCA of 164°. The resulting superhydrophobic cotton fabric demonstrated remarkable resistance to various solvents such as NaOH (1 M), HCl (1 M), coffee, etc., as well as UV radiation and abrasion tests, maintaining WCAs above 150°.

2.7.4.3. Other Chemical Synthesis Methods

There are other surface modification methods that have been used to prepare superhydrophobic surfaces. One such method is click chemistry which refers to reactions that yield high-purity products with excellent selectivity through the formation of carbon-hetero bonds under mild reaction conditions.¹³² The term "click chemistry" was coined by Nobel laureate K. Barry Sharpless in 2001 to describe reactions that are highly modular, orthogonal (compatible with each

other), and can be performed with high yields and minimal byproducts.¹³² Thiol-ene click chemistry is commonly used for modification of surfaces.^{133,134} It is a specific subset of click chemistry that involves the reaction between thiols (compounds containing a sulphur-hydrogen bond, denoted as -SH) and alkenes (compounds containing a carbon-carbon double bond, denoted as -C=C-).^{135,136} In this reaction, the thiol group reacts with the carbon-carbon double bond of the alkene, leading to the formation of a carbon-sulphur bond and the release of a hydrogen atom. Peng et al.¹³² prepared superhydrophobic melamine sponge by functionalisation with PDMS through UV-assisted thiol-ene click reaction, achieving WCA of 156.2°. In a recent study, Chen et al.¹³⁷ used one-step thiol-ene click chemistry to prepare superhydrophobic cotton fabric using 1-Tetradecanethiol, vinyltrimethoxysilane and 2,2-dimethoxy-2-phenylacetophenone. The prepared fabric achieved WCA of 159° and it was resistant to UV, acids, acetone, and water washing.

Another method often used is reversible addition-fragmentation chain transfer polymerisation (RAFT), which is a controlled radical polymerisation technique used to synthesise polymers with well-defined structures.¹³⁸ RAFT polymerisation falls in class of reversible deactivation radical polymerisation (RDRP) methods.¹³⁹ In RAFT polymerisation, a chain transfer agent (CTA) is used to regulate the polymerisation process, allowing for precise control over the molecular weight, composition, and architecture of the resulting polymer chains.^{138,139} For example, Xu et al.¹⁴⁰ employed RAFT polymerisation to synthesise a di-block copolymer, poly[(methyl methacrylate)-b-(trifluoroethyl methacrylate)] (PMMA-b-PTFMA), which was subsequently used to modify cotton fabric. The study utilised mist treatment with the polymer dissolved in acetone to treat the fabric, resulting in a superhydrophobic surface with a WCA of 140°. The PMMA segment of the copolymer served to covalently bond the copolymer to the cotton fabric, while the PTFMA component introduced superhydrophobic features. Interestingly, although the modified cotton fabric lost its superhydrophobicity after 60 laundering cycles and 2000 abrasion cycles, achieving WCAs of 140° and 148°, respectively, its high self-healing property allowed the fabric to regain superhydrophobicity.

Atom transfer radical polymerisation (ATRP) is another reversible deactivation radical polymerisation (RDRP) method commonly used for superhydrophobic material modifications.^{139,141} ATRP utilises transition metal catalysts, typically copper complexes, to facilitate the reversible activation and deactivation of dormant polymer chains, thereby enabling controlled polymerisation.^{142,143} Wang et al.¹⁴⁴ and Li et al.¹⁴⁵ both employed this technique to fabricate superhydrophobic cotton wool and cotton fabric, respectively, achieving WCAs exceeding 154°. Li et al. further demonstrated the durability of fabrics prepared using this method, maintaining a high WCA of 149° even after 30 accelerated washing cycles and 800 abrasion cycles against sandpaper.

Another technique often used for creating superhydrophobic surfaces is chemical vapour deposition.^{146–148} CVD is a process used to create thin films and coatings by chemical reactions that occur at the surface of a substrate material.¹⁴⁹ In CVD, precursor gases are introduced into a chamber containing the substrate material, and upon reaching the surface, they undergo chemical reactions or decompose to deposit a thin layer of material onto the substrate.¹⁵⁰ In a recent study, Kundu et al.¹⁵¹ used plasma enhanced chemical vapour deposition to coat cotton fabrics with amorphous carbon nanoparticles achieving WCA of 130°. WCA was increased beyond 150° with stearic acid treatment.

2.7.4.4. Application in Oil-water Separation

Superhydrophobic materials exhibit exceptional oleophilic properties.¹⁵² Therefore, these materials represent a promising avenue for oil-water separation through sorption processes, owing to their innate ability to repel water while selectively absorbing oils. As already mentioned in section 2.7, these materials typically consist of low surface energy compounds and intricate surface structures that create air pockets, preventing water intrusion while facilitating the uptake of oils. Superhydrophobic materials hold great promise for addressing oil spill cleanup, wastewater treatment, and industrial oil-water separation, with continued research aiming to optimise their performance and environmental sustainability.^{153–155} Utilising the principle of selective surface

tension differentiation between oil and water, the materials can be categorised as either filters/filtration membranes or sorption material.^{156,157} The filtration membrane selectively allows the permeation of either oil or water while repelling the alternative phase, thereby achieving a separation between the two. Meanwhile, the sorption material exhibits the ability to preferentially absorb/adsorb either water or oil on its surface, consequently inhibiting the penetration of the opposing phase into the sorbent material. These materials have been utilised for separating both immiscible oil-water mixtures and oil-in-water emulsions,^{152,158} which are common forms of FOGs found in food industries and other FOG source points.

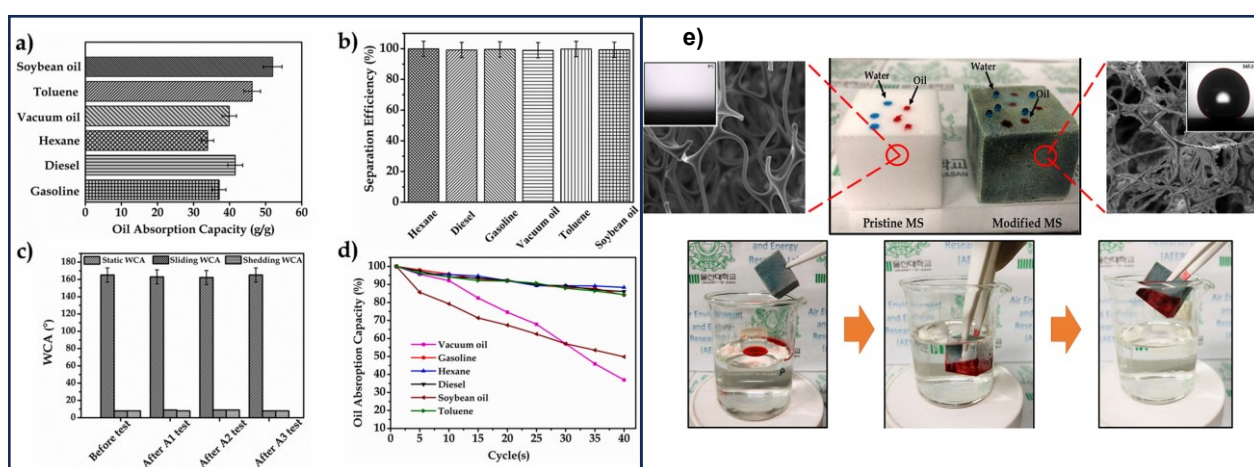


Figure 2.12 Oil absorption capacity of six types of oils, (b) separation efficiency of the modified melamine sponge with different types of oils, (c) stability test for superhydrophobic melamine sponge and (d) Reusability test of the modified melamine sponge, (e) morphology, wettability, and oil-water separation properties of the modified sponge. Reproduced with permission from ref.¹⁵⁹. Copyright 2021, Elsevier.

Nguyen-Dinh et al.¹⁵⁹ fabricated a superhydrophobic melamine sponge with a WCA of 160°, using copper oxide and stearic acid for oil-water separation (Figure 2.12). The prepared sponges exhibited remarkable separation performance, achieving efficiencies above 99% for various oils. Additionally, they discovered that the sorption capacities were high, ranging from 32 to 52 times the weight of the sponge. In another study, Li and Guo prepared a superhydrophobic melamine sponge by adhering nano-graphite flakes with PDMS, followed by silanisation with hexadecyltrimethoxysilane.¹⁶⁰ This sponge effectively removed toluene and methylene chloride from both water surface and underwater, respectively. The sponge also displayed high sorption capacities (> 20 g/g) for different oils including rapeseed oil. More importantly, the sponge

maintained consistent oil sorption capacities during a 10-cycle sorption-squeezing test, and even after 100 reuse cycles. Furthermore, the sponge successfully separated surfactant-free toluene oil-in-water emulsions by immersing a piece of sponge in the emulsion and vigorously shaking it.

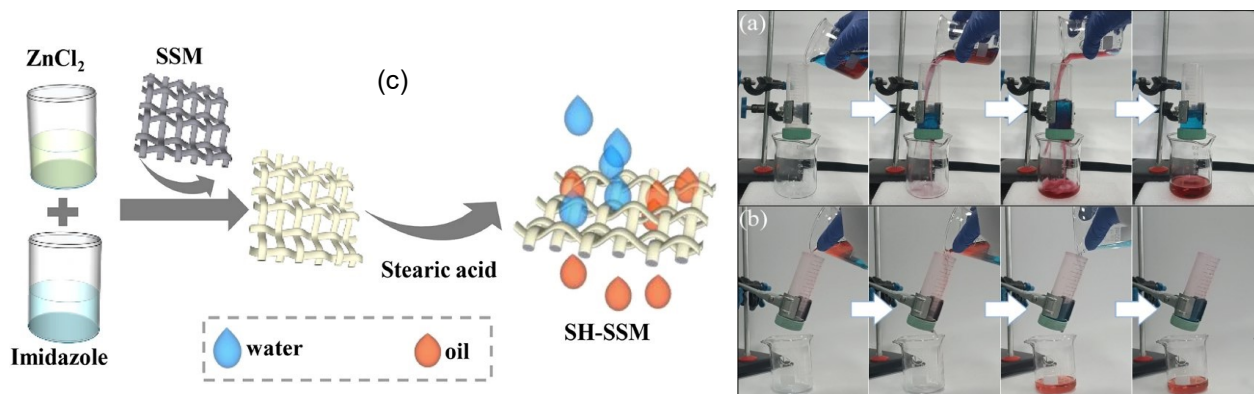


Figure 2.13 Illustration of the fabrication of superhydrophobic stainless steel mesh (c), Images showing oil-water separation (a) heavy oil-water and (b) light oil-water separation. Adapted from ref.¹⁶¹ which is an open access paper.

Xu et al.¹⁶¹ fabricated a superhydrophobic stainless steel mesh using zinc stearate self-assembly for separating various oil-water mixtures (Figure 2.13c). The separation process employed a filtration method, allowing only oil to pass through the mesh while rejecting water (Figure 2.13a,b). To separate light oils, the separation unit was tilted to ensure contact of oil with the mesh filter. The prepared mesh filter achieved over 99.9% separation efficiency for both heavy and light oils, with high fluxes exceeding $1.7 \times 10^5 \text{ L m}^{-2} \text{ h}^{-1}$. Flux of the filter is defined as the flow rate of the filtrate collected per unit area of the filter. Furthermore, the mesh exhibited superior reusability, maintaining over 97% efficiency even after 20 separation cycles. Several studies have demonstrated the efficacy of superhydrophobic materials in separating surfactant-free and surfactant-stabilised oil-in-water emulsions.^{156,158,162–164} Despite their effectiveness in demulsifying these emulsions, superhydrophobic materials are commonly utilised for separating water-in-oil emulsions.^{157,165,166}

2.8. Superhydrophilic and Superamphiphilic Materials

Superhydrophilic surfaces possess an extraordinary affinity for water causing water droplets to spread out extensively upon contact. These surfaces can be achieved through various methods like surface treatments, coatings, or nano-structuring, which are similar techniques as described in

the above section 2.7.4 for superhydrophobic materials. Superhydrophilic surfaces are gaining attention for their potential in emulsion separation processes, crucial for industries ranging from wastewater treatment to food processing. Due to their strong affinity for water, they offer a promising avenue for selectively separating water from oil-in-water emulsions.¹⁶⁷ By utilising superhydrophilic membranes/filters or coatings, researchers are exploring methods to allow water to pass through while repelling oil droplets, thereby achieving efficient separation. Additionally, superhydrophilic coatings promote the coalescence of water droplets, facilitating their separation from the emulsion.

Wang et al.¹⁶⁷ developed a superhydrophilic cellulose sponge through the dissolution and regeneration of cellulose powder. This green synthesis approach yielded a sponge with underwater superoleophobic properties, achieving over 99.9% separation efficiency for surfactant-stabilised toluene oil-in-water emulsion. Another class of materials frequently employed for emulsion separation are superamphiphilic materials.^{168–170} Superamphiphilic refers to materials that exhibit extreme dual affinity towards both hydrophobic (water-repelling) and hydrophilic (water-attracting) substances. These materials possess surface properties that enable them to interact strongly with both water and non-polar substances such as oils or organic solvents.

For example, Lei and Guo electroplated copper onto stainless steel surface, followed by oxidation to form copper hydroxide nanoneedles, resulting in a superamphiphilic stainless steel.¹⁷¹ This material demonstrated remarkable adaptable wettability, displaying superhydrophilic/oleophobic properties with oil-in-water emulsion feeds, allowing water filtration while repelling oil. Conversely, it exhibited the opposite behaviour with water-in-oil feeds. In a separate study, Zhu et al.¹⁷² devised superamphiphilic copper foams through a one-step spray coating process, employing hydroxyl-functionalised multi-wall carbon nanotubes and melamine formaldehyde for oil-water separation (Figure 2.14). The selectivity of these foams towards water or oil was regulated by prewetting with either water or oil, respectively. The resulting foam demonstrated efficient

separation of oil and water via gravity-driven filtration, achieving fluxes surpassing $5000 \text{ L m}^{-2} \text{ h}^{-1}$ and separation efficiencies exceeding 95%.

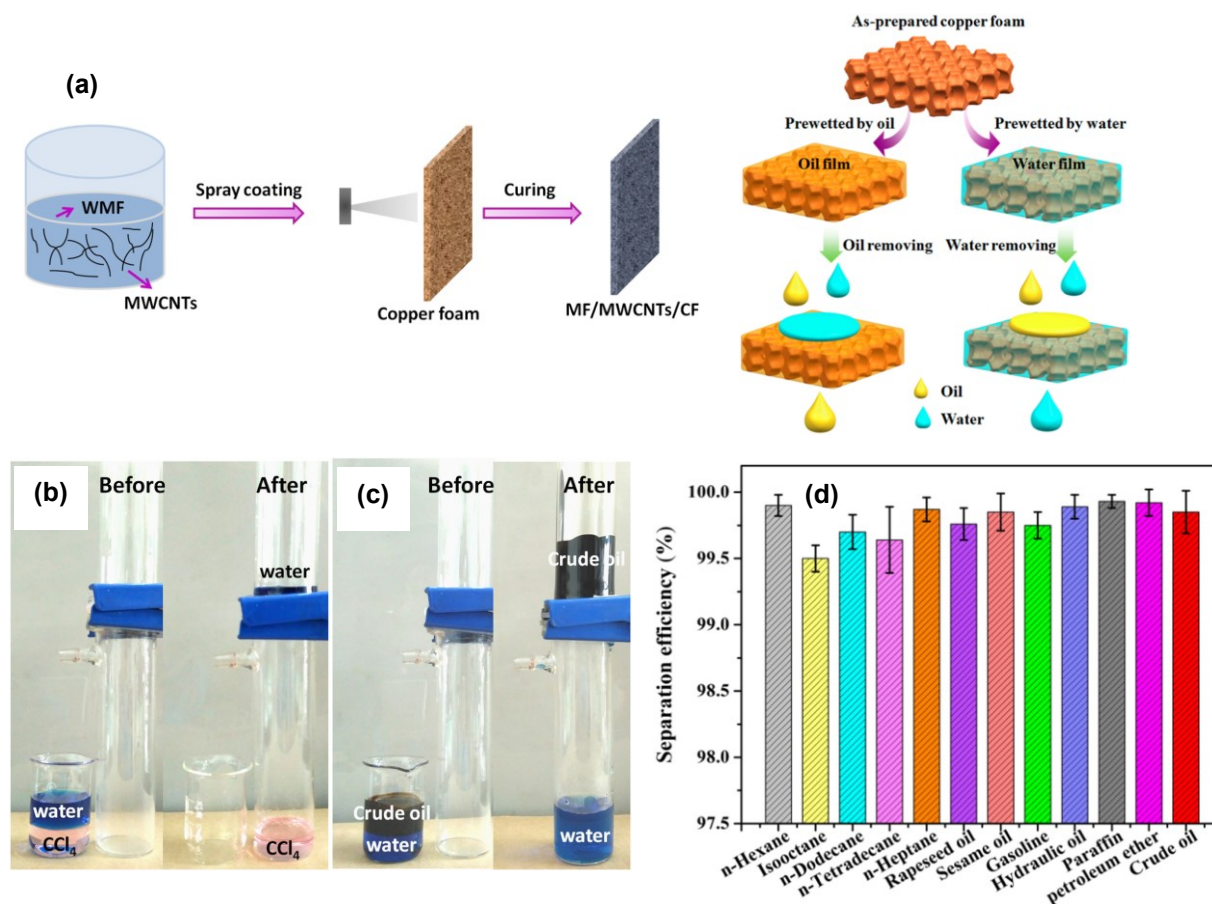


Figure 2.14 (a) Schematic diagram showing the preparation of superamphiphilic copper foam for selective separation of oil-water mixtures, (b, c) the oil-water separation property of the prepared copper foam, (d) the separation efficiency of the copper foam for various of oil-water mixtures. Adapted from ref.¹⁷² with permission from Elsevier (© 2017 Elsevier B.V.)

2.9. Materials with Switchable Wettability

These materials possess the remarkable ability to dynamically alter their interaction with liquids, transitioning between hydrophobic and hydrophilic states in response to external stimuli.¹⁷³ They utilise a range of mechanisms including responsive polymers, liquid-infused surfaces, chemical modification, etc to achieve reversible changes in surface energy and wettability.^{173–175} These materials offer the potential for more efficient, cost-effective, and environmentally friendly oil-water separation. By switching between hydrophilic and hydrophobic states, the materials can selectively attract or repel oil and water phases, facilitating their separation. pH-responsive materials represent a significant mechanism commonly used for switching wettability.^{176–182} By

incorporating pH-responsive functional groups such as carboxylic acids, amines, or phosphates into the material structure, the surface properties can be tuned to switch between hydrophobic and hydrophilic states.

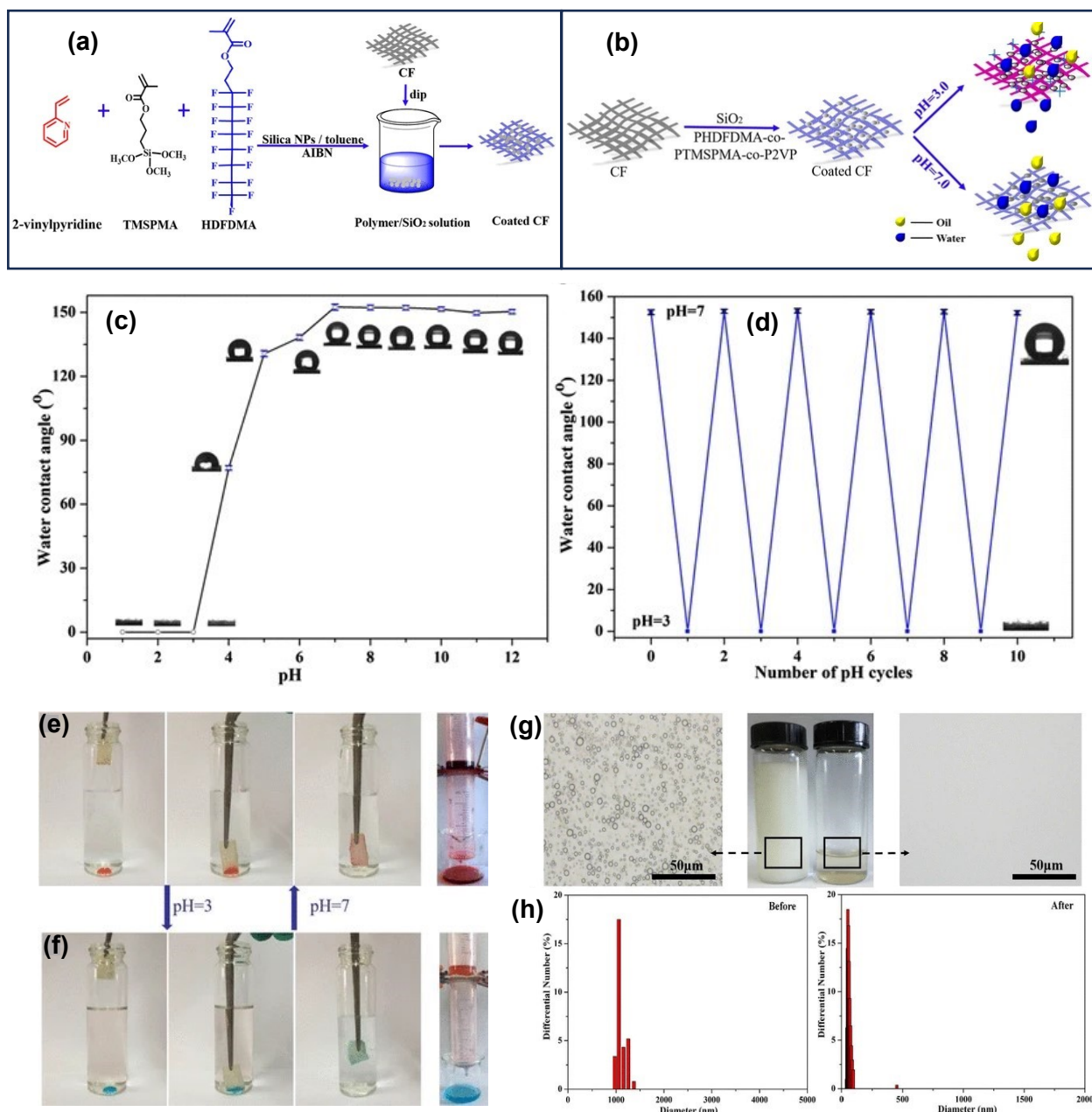


Figure 2.15 (a) synthesis of pH-responsive cotton fabric, (b) mechanism of pH responsive cotton fabric, (c) changes WCA with pH (d) the WCA transition cycles of coated cotton fabric via pH treatment, (e) photographs showing removal of CHCl₃ (dyed with Sudan III) and image of continuous separation of oil-water mixture, (f) removal process of water (dyed with methylene blue) sinking at the bottom of toluene and continuous separation of oil-water mixture, (g-h) images showing emulsion separation. Adapted from ref.¹⁸³ with permission from Springer (© Springer-Verlag GmbH Germany, part of Springer Nature 2018).

For instance, Wang et al.¹⁸³ devised a method to create pH-controlled switchable wettability on cotton fabric (Figure 2.15). They achieved this by coating the fabric with silica nanoparticles

and a copolymer of poly(heptadecafluorodecyl methacrylate-*co*-3-trimethoxysilylpropyl methacrylate-*co*-2-vinylpyridine) (PHDFDMA-*co*-PTMSPMA-*co*-P2VP). The pH-responsive copolymer, PHDFDMA-*co*-PTMSPMA-*co*-P2VP, was synthesised via radical polymerisation of TMSPMA, 2-vinylpyridine (2-VP) and HDFDMA using α,α -azobis-(isobutyronitrile) (AIBN) in toluene under nitrogen atmosphere. It was observed that the cotton fabric exhibited a superhydrophilic surface when immersed in an acidic solution (pH = 3), which transitioned to superhydrophobicity upon immersion in a neutral solution (pH = 7). This fabric demonstrated exceptional efficiency (> 99.8%) in separating oil-water mixtures, ternary oil-water-oil mixtures, and both oil-in-water and water-in-oil surfactant-stabilised emulsions. Additionally, solvents can be utilised to switch wettability.^{173,184} For example, Zhang et al.¹⁸⁵ developed superhydrophobic cotton fabric with switchable wetting to superhydrophilicity through immersion in ethanol. The fabric was coated with a composite of ZIF-8 MOF nanoparticles and polyvinylidene fluoride, followed by modification with PDMS. This fabric exhibited excellent performance in oil-water separation, achieving over 98.6% separation efficiency and a flux exceeding 15 300 L m⁻² h⁻¹. Other commonly employed external stimuli include, but are not limited to, temperature, gases, and electric fields.^{173,186,187}

2.10. Summary

The project's objective, as outlined in Chapter 1, stemmed from the research gaps identified in the literature. As mentioned earlier, the materials reviewed in existing studies have not been directly applied as an alternative solution for removing FOGs from wastewater to prevent fatberg formation. Most of the studies primarily focus on petroleum oils and other organic solvents such as toluene. Therefore, this project primarily targets cooking oils and any oily wastewaters recovered from domestic households to simulate actual FOG-laden wastewater.

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Chapter 3. Methodology

In the upcoming chapters, each study will be accompanied by its distinct "Methodology" section tailored specifically to its requirements. Nevertheless, to prevent repetition in subsequent sections, this part will encompass shared materials and characterisation techniques employed across chapters 4-7.

3.1. Materials

Cotton wool, oil red O, TEOS ($\geq 99\%$), sodium dodecyl sulfate (SDS) ($\geq 99\%$), methylene blue solution, sodium chloride (NaCl) ($\geq 99.0\%$), dichloromethane ($\geq 99.9\%$), octyltrimethoxysilane (OTMS) (96%), propyltrimethoxysilane (PTMS) (98%), (3-aminopropyl)trimethoxysilane (APTMS) (97%) and anhydrous alkanes (C_6-C_{10}) ($\geq 99\%$) were purchased from Sigma Aldrich (Gillingham, UK). Ethanol ($\geq 99.8\%$), acetone ($\geq 99.8\%$), hydrochloric acid (HCl) (37%), sodium hydroxide (NaOH) pellets, ammonia solution (28%), toluene ($\geq 99.5\%$) and ODTMS (90%) were purchased from VWR (Lutterworth, UK). De-ionised (DI) water was provided by the PURELAB Chorus 1 (ELGA LabWater) water purification system. Cooking oils (vegetable, rapeseed, sunflower, olive, and sesame oil) were sourced from a local supermarket.

All chemicals and reagents were used without further purification unless stated otherwise.

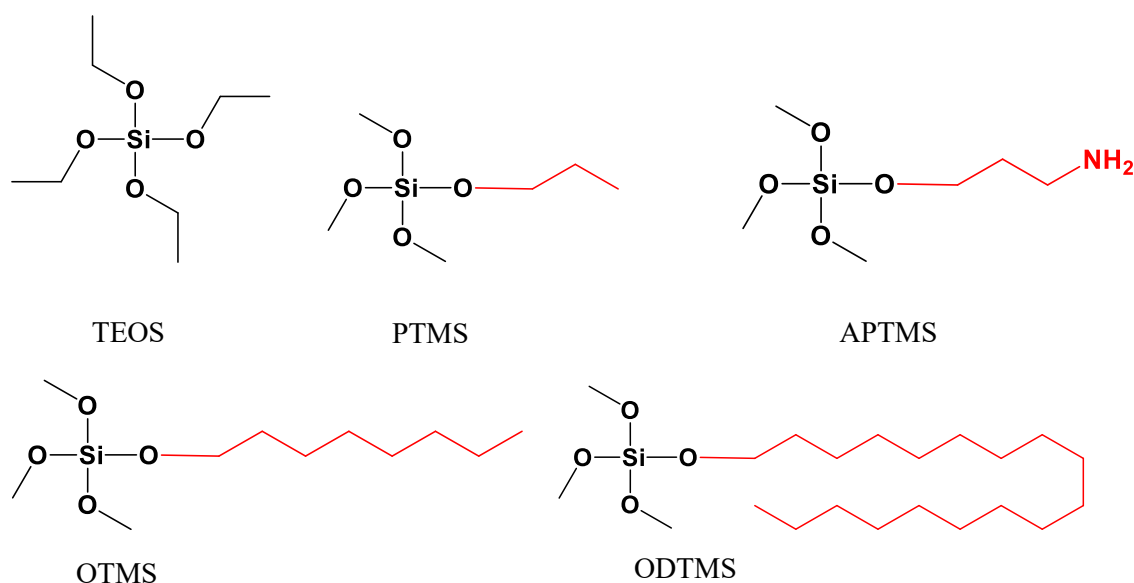


Figure 3.1 Chemical structure of the silica precursor and silanes used.

3.2. First Pre-treatment Stage of Cellulosic Materials

Cotton wool was washed in acetone twice and squeezed to remove excess acetone. This was followed by drying in an oven at 60 °C for 1 h.

3.3. Characterisation of Samples

3.3.1. Morphology

The morphology of samples was assessed using a scanning electron microscope (SEM) on a Leo Gemini 1525 scanning electron microscope (Carl Zeiss AG, Germany) at 5 kV. Prior to analysis, a small sample quantity was affixed to carbon conductive adhesive tape and coated with a 15 nm layer of chromium using a Q150T turbomolecular pumped coating system (Quorum Technologies Ltd., UK). The coating is to prevent the charging effect in SEM caused by non-conductive materials resulting in anomalous contrast of the observed specimen's images.^{1,2} The charging effect or charge build up in the sample is caused by accumulation of electrons due to electrical insulation features of the sample, leading to no dissipation of charge to the ground.^{2,3} As such leading to blurred image regions and beam drift.

The SEM employs a focused beam of accelerated electrons to investigate the surface of a specimen. This electron beam interacts with the specimen, generating secondary electrons (SE) and backscattered electrons (BSE).⁴ Secondary electrons provide topographical details, while backscattered electrons offer compositional information based on the atomic number of elements. As the electron beam scans the specimen's surface, detectors collect the emitted signals, enabling the formation of high-resolution images.

3.3.2. Chemical Analysis

3.3.2.1. Fourier Transform Infrared Spectroscopy

The bulk sample chemical structure was confirmed using Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) in an Agilent Technologies Cary 630 FTIR. All spectra were collected using 64 scans in the wavenumber range 4000-500 cm⁻¹ with a resolution

of 4 cm^{-1} . Samples were placed and compressed onto a diamond crystal to record the spectra following the collection of the background using the same analysis parameters. This crystal enables total internal reflection, causing the infrared light to penetrate only a short distance into the sample. As the infrared beam interacts with the sample, molecular bonds absorb specific frequencies of light, leading to vibrational changes.⁵ A detector measures the intensity of the infrared beam after it has interacted with the sample, resulting in a spectrum which provides a unique fingerprint of the sample's molecular composition.

3.3.2.2.X-ray photoelectron spectroscopy

For the evaluation of surface chemistry, X-ray photoelectron spectroscopy (XPS) was employed with the K-Alpha+ system (Thermo-Fisher Scientific Inc., USA), operating at a base pressure of 2×10^{-9} mbar. The system features an Al K α monochromated X-ray source ($h\nu = 1486.6$ eV) operated at 6 mA and 12 Kv along with a 180° double-focusing hemispherical analyser equipped with a 2D detector.⁶ The X-ray source had a spot size of $400\text{ }\mu\text{m}^2$, facilitating maximum counts. Survey spectra and high-resolution spectra were acquired with pass energies of 200 eV and 20 eV, respectively.⁷ The subsequent quantitative analysis was conducted using Avantage software.

XPS operates by irradiating a sample with X-ray photons, inducing the photoelectric effect and ejecting inner-shell electrons.⁸ The kinetic energy of these emitted electrons is analysed, providing information about the binding energy and, consequently, the elemental composition of the sample. By utilising an energy analyser, XPS separates electrons based on their kinetic energy, producing a spectrum that reflects the abundance of emitted electrons at different energy levels.⁹ Peaks in the spectrum correspond to specific binding energies of elements present in the sample. Through careful analysis of the XPS spectrum, specific elements can be identified, determine their chemical states, and gain insights into the surface composition and electronic structure of materials.

3.3.3. Thermal Properties

Thermogravimetric analysis (TGA) was carried out using STA 449C (Netzsch, Germany) from 30 to $800\text{ }^\circ\text{C}$ in nitrogen and/or air atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Around 10 mg

of sample was loaded into the aluminium oxide crucible pans. The samples were burnt under a flowrate of 60 mL/min of the analysis gas (nitrogen or air) with 20 mL/min of protective nitrogen gas. As the sample undergoes heating, the TGA machine continuously measures its weight, producing a TGA curve that illustrates changes in weight relative to temperature.

3.3.4. Wetting Properties

Static WCA measurements were conducted in 590 goniometer/tensiometer (Ramé-hart Instrument Co., USA) using a sessile drop method with 6 μ L droplet. Samples were attached to a glass slide using a double-sided tape. The samples were then compressed in between two slides to create a flat surface. 100 measurements were taken at one location and this was repeated for 2 other locations on the sample. The WCA was then calculated as an average of all the collected measurements.

The goniometer captures images to calculate the contact angle formed between the liquid droplet and the solid surface. Simultaneously, the tensiometer measures the surface tension by analysing the droplet's shape on the solid surface. The instrument's software processes the data and calculates both contact angle and surface tension, providing insights into the wettability and interfacial properties of materials.

3.3.5. Surface Energy Analysis

Surface energy of cotton wool was determined using the infinite dilution method with 3% probe surface coverage in an inverse gas chromatography (IGC) surface energy analyser (Surface Measurement Systems, UK). ~50 mg of the sample was packed into a silanized glass column (length = 300 mm, internal diameter = 3 mm). The dispersive (γ_S^d) component of surface energy, using the Schultz approach,¹⁰ was determined from the retention behaviour of the n-alkane probes (decane, nonane, octane, heptane, and hexane). Furthermore, the specific (acid-base) (γ_S^{ab}) component of surface energy was calculated using the Della Volpe approach^{11,12} from the retention behaviour of the polar probes (dichloromethane and toluene). All the experiments were conducted at 30 °C and 0% relative humidity after conditioning the sample under the same conditions for 2 h.

All the theoretical calculations involved in IGC analysis are discussed extensively in the literature,^{10,13,14} and some relevant ones are summarised below. Methane gas is used as a non-interacting reference gas with a retention time of t_{ref} . For every organic probe utilized, the net retention volume (V_N) of the carrier gas necessary to elute the injected probe molecules through the column is determined by the following formula:

$$V_N = F \cdot \frac{J}{m} \cdot (t_{probe} - t_{ref}) \cdot \frac{T}{293.15} \quad (3.1)$$

where F is the carrier gas volumetric flow rate, J is the James-Martin gas compressibility correction factor, m is the mass of a solid sample packed in the column, T is the sample column temperature and t_{probe} is the elution time of the organic probe used.

The Gibbs free energy of adsorption of the probe molecules can be deduced from V_N using:

$$\Delta G_a = -RT \ln(V_N) + C \quad (3.2)$$

here, R is a gas constant and C is a constant. The free energy of adsorption is often correlated to work of adhesion by:¹¹

$$\Delta G_a = -N \cdot a \cdot W_a \quad (3.3)$$

where W_a is the work of adhesion between the gas probe and the solid phase, N is the Avogadro's number, a is the molecular surface area of the probe. W_a can be divided into two contributions, the one from the Lifshitz–Van der Waals ($\gamma_{s,l}^d$) and the polar interactions ($\gamma_{s,l}^{ab}$). For non-polar probes, the W_a is dominated by dispersive interactions over polar interactions, therefore the $\gamma_{s,l}^{ab}$ is negligible¹⁵. Under the same conditions, Fowkes defined W_a as:^{15,16}

$$W_a^d = 2(\gamma_s^d \cdot \gamma_l^d)^{0.5} \quad (3.4)$$

where γ_s^d is the dispersive surface free energy of the solid and γ_l^d is the Lifshitz-Van der Waals dispersive surface free energy of the probe. Then combining equations (2), (3) and (4) to obtain:

$$-\Delta G_a^d = RT \ln(V_N) = 2N \cdot a \cdot (\gamma_s^d)^{0.5} (\gamma_l^d)^{0.5} + C' \quad (3.5)$$

By plotting a linear regression between the $RT\ln(V_N)$ vs $a(\gamma_l^d)^{0.5}$, the slope of the line $[2N \cdot (\gamma_s^d)^{0.5}]$ can be used to determine γ_s^d .

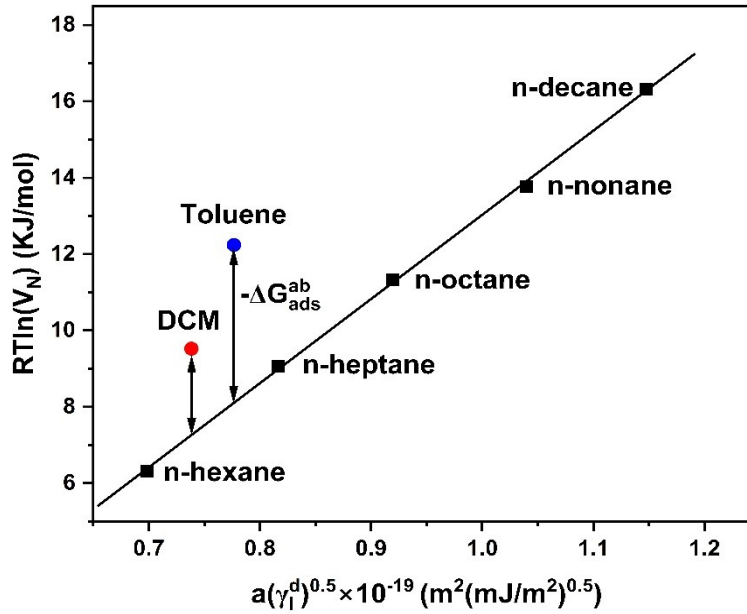


Figure 3.2 Typical free energy of adsorption for C₆-C₁₀ n-alkane probes (n-alkane line) and free energy of adsorption of different polar probes.

The free energy of adsorption (ΔG_a) for polar probes includes contributions from both dispersive interactions and polar/acid-base interactions (equation 3.6).¹³

$$\Delta G_a = \Delta G_a^d + \Delta G_a^{ab} \quad (3.6)$$

By employing the linear regression graph of alkanes, ΔG_a^{ab} for any polar probe can be calculated as the offset difference of ΔG_a from the alkane line (Figure 3.2). Using Van Oss-Good theory,^{13,17} the acid-base (also known as the specific surface energy) free energy can be determined using the following equations:

$$\Delta G_a = 2N \cdot a \cdot [(\gamma_l^+ \gamma_s^-)^{0.5} + (\gamma_s^+ \gamma_l^-)^{0.5}] \quad (3.7)$$

$$\gamma_s^{ab} = 2(\gamma_s^+ \gamma_s^-)^{0.5} \quad (3.8)$$

where γ^+ is the electron-acceptor (acidic) parameter and γ^- is the electron-donor parameter of the surface energy, with subscripts indicating solid (s) or liquid (l). The total surface energy of the solid is then calculated as the sum of γ_s^{ab} and γ_s^d .

3.4. Durability Study

Chemical durability was evaluated by immersing the modified cotton in various solvents, including acetone, hexane, toluene, dichloromethane (DCM), hot DI-water (HW) (60 °C), and NaCl (3 M), for 24 h. After each test, the samples were washed twice in ethanol and dried before further analysis. The durability of the cotton samples was then assessed using WCA measurements. The pH durability was examined by immersing the modified cotton in NaOH solutions (pH = 8 to 13), HCl solutions (pH = 2 to 6) and DI water (PH = 7). To test the durability of the modified cotton under laundry conditions, the modified cotton was stirred at 300 rpm and 40 °C in a 0.15 wt% detergent solution for 45 min using a magnetic stirrer. Subsequently, the detergent was rinsed off with DI water three times and once with acetone. This constituted one full laundry cycle, which was repeated for 36 wash cycles. The cotton was dried between the cycles and WCA measurements were taken after every 6 cycles. For assessing mechanical durability, abrasion testing was performed on a sandpaper (Figure 3.3). The cotton was pressed onto the sandpaper using a 1 kg weight, and the weight was rotated, with each full rotation considered as one test cycle. For each rotation, it was ensured that the weight completely covered the entire cotton sample. WCA measurements were conducted after every 6 cycles for a total of 36 cycles.

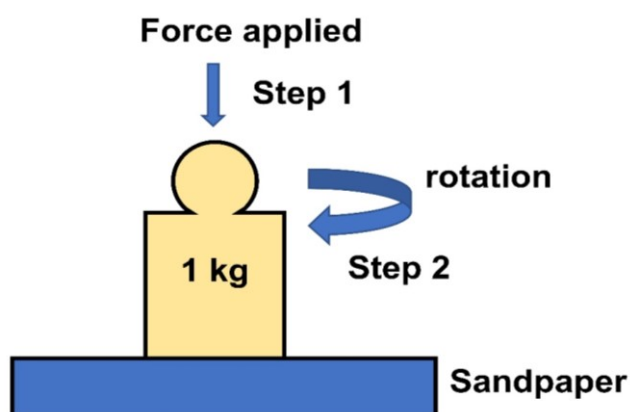


Figure 3.3 Abrasion testing set-up.

3.5. Water Sorption

Water sorption on the cotton was tested by immersing samples in water for 5 h. Subsequently, the water-soaked cotton was removed and placed on a stainless-steel filter mesh to remove excess water before weighing. The samples were left on a filter until no water droplets were observed dripping below it. The water sorption capacity (S_w) was calculated using the following equation:

$$S_w(g/g) = \frac{w_1 - w_0}{w_0} \quad (3.9)$$

here, w_0 and w_1 represent the masses of the cotton before and after water sorption, respectively. To prevent modified cotton samples from floating on the water surface, they were deliberately submerged underwater during the testing process.

3.6. Oil-water Separation

Initially, the maximum oil sorption capacity (S_{max}) for different oils in a pure oil system was determined. A piece of modified cotton was left to soak in pure oil for 1 h, after which it was removed and placed on a steel mesh to remove excess oil before weighing the sample. The oil sorption capacities were then calculated using the following equation:

$$S_{max}(g/g) = \frac{m_2 - m_1}{m_1} \quad (3.10)$$

where m_1 and m_2 are the initial and final masses of cotton, respectively. To assess the oil-water separation capabilities of the prepared cotton, 2 mL of oil was added to 20 mL of DI water. This was followed by adding ~0.1 g of modified cotton to the mixture and leaving it for 5 min. The mass of cotton used was determined based on the maximum sorption capacity results. Consequently, the cotton mass used provided excess capacity beyond the oil mass added to water, ensuring that the sorption capacity of the cotton was not a limiting factor. The oil-soaked cotton was then removed, and the remaining oil was quantified using a UV-Vis spectrometer (nanodrop 2000c, Thermo-Fisher Scientific Inc., USA) after oil extraction with 5 mL of hexane (see calibration curves in Figure 3.4). The separation efficiency (E) was calculated from:

$$E(\%) = \left(\frac{v - v_r}{v} \right) \cdot 100\% \quad (3.11)$$

where v and v_r are the initial and residual volume of oil, respectively. In the visualisation experiments, oil was dyed with oil red O before being added to water and images were taken at different stages.

3.6.1. UV-Vis Spectrometer

The UV-Vis spectrometer operates based on the principle of measuring the absorption of ultraviolet and visible light by a sample. A beam of light, covering a range of wavelengths in the UV and Visible regions, is emitted through the sample. The molecules in the sample absorb light at specific wavelengths, causing electronic transitions and elevating electrons to higher energy levels.¹⁸

A detector measures the intensity of the transmitted light, and the resulting spectrum is generated by plotting absorbance values against corresponding wavelengths. The absorbance is related to transmittance as the negative logarithm of transmittance. Peaks and troughs in the spectrum reveal information about the sample's molecular structure and composition. By comparing with a reference measurement, variations in the light source and detector sensitivity are accounted for. The measured absorbance can be related to the sample concentration using the Lambert-Beer law which allows for the determination of concentrations using UV-Vis spectrometer.¹⁸ Lambert-Beer law relates the attenuation of light to the concentration and extinction coefficient of the sample. This is summarised by equation 3.12.

$$A = \varepsilon \cdot c \cdot d \quad (3.12)$$

where A is absorbance, ε is the sample's extinction coefficient, c and d are the sample concentration and path length, respectively. According to the Lambert-Beer law, the calibration curves should have a y-intercept of 0, meaning the best-fit lines pass through the origin (0,0). However, the y-intercepts determined for the calibration curves were small enough that they did not significantly affect the oil concentration measurements. Therefore, the calibration curves were used directly without adjusting for the intercept.

Blank measurements were conducted using hexane before analysing the samples. The absorbance at the wavelength of 260 nm (and 230 nm for olive oil) was utilised to establish the calibration curves (Figure 3.4).

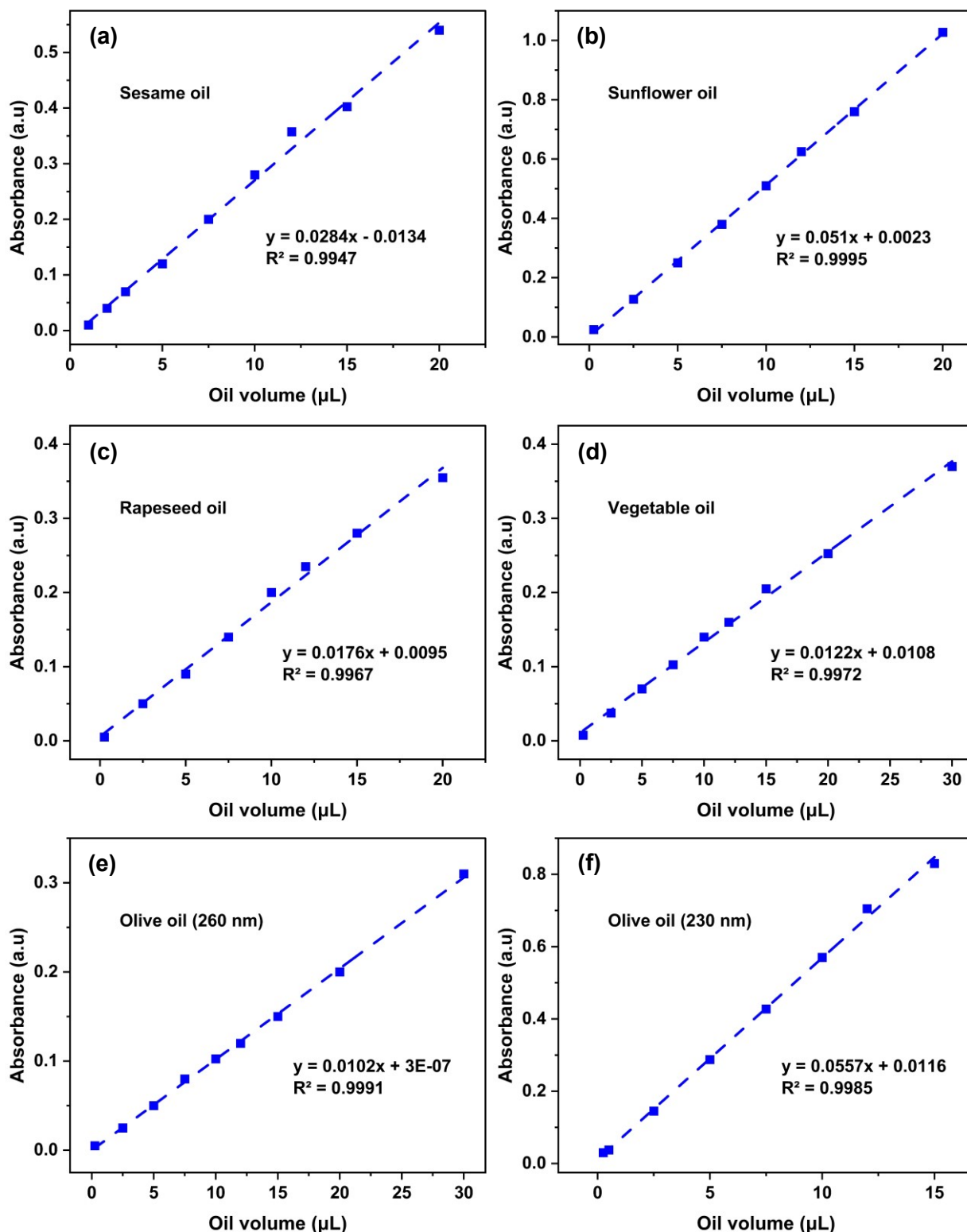


Figure 3.4 Calibration curves for different cooking oils in 5 mL hexane using UV-Vis spectrometer.

The calibration curves for cooking oil in hexane were established using a quartz cuvette capable of measurements within the 200-400 nm range with high transmittance. Various volumes of oil were directly added to hexane to create these curves. However, the oil extraction efficiency of hexane was determined using 10 μL of olive oil in 20 mL of water. The oil was extracted with 5 mL of hexane, and using the calibration curve the extraction efficiency was calculated to be 81.4%. This efficiency value was assumed to remain constant across different oils. For oil-water separation experiments, the volumes determined from the calibration curves were adjusted by dividing them by the extraction efficiency to account for the unextracted oil. In cases where the absorbance exceeded 1, the experiments were repeated with a diluted sample, and the dilution factor was used to determine the actual volume of oil in the initial sample. This approach ensured more accurate results for samples with higher absorbance values.

3.6.2. Total Organic Carbon (TOC) Analyser

TOC analysis is a method used to measure the amount of organic carbon in a sample. It is commonly used in environmental science, water treatment, and industrial applications to assess the cleanliness or pollution levels of water, soil, and other materials. The analysis involves first oxidising the organic carbon to carbon dioxide which is then quantified using a non-dispersive infrared (NDIR) detector.¹⁸ The TOC analyser uses persulfate and UV light to transform organics into carbon dioxide.¹⁹ Any inorganic carbon is converted to carbon dioxide by acidifying the sample with phosphoric acid.¹⁹ The TOC analyser was used in Chapter 6 to determine the oil composition in the samples after the surfactant-free emulsion separation. It was not used in Chapter 7 due to the presence of surfactant-stabilised emulsions, which could lead to an overestimation of oil concentration if the surfactant filters into the filtrate. Instead, UV-Vis spectroscopy was employed because the SDS surfactant used was not detected by the UV-Vis spectrometer at the given concentration.

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Chapter 4. Preliminary Experiments Using Chicken Eggshell Waste and Silica Nanoparticles

Abstract

Superhydrophobic silica and chicken eggshell powders were investigated as adsorbents for oil-water separation. Hydrophobic silica particles were prepared using both post-grafting and one-pot surface modification methods, employing hydrophobic silanes such as PTMS, OTMS, and ODTMS. Concurrently, superhydrophobic eggshell powder was synthesised using a dry mechanochemical synthesis method, incorporating stearic acid as a modifying agent. The resulting materials exhibited superhydrophobicity ($\text{WCA} > 156^\circ$), with the exception of PTMS-modified silica ($\text{WCA}=143.9^\circ$). These prepared surfaces demonstrated remarkable oil-water separation capabilities, achieving an 85.7% separation efficiency for eggshells and over 90% for silica-based powders. However, despite their efficacy, the powders pose challenges in practical applications, including challenging post-separation recovery and low sorption capacity. To address these issues, cellulosic materials, especially cotton, were introduced in this research. Nevertheless, these materials provide an economical and straightforward solution for oil-water separation applicable across various industries.

4.1. Introduction

Silica nanoparticles have garnered considerable attention in the realm of nanotechnology and materials science due to their unique properties and versatile applications.¹ The distinctive characteristics of silica, such as its high surface area, tuneable porosity, and excellent biocompatibility, make silica nanoparticles a compelling choice for a wide range of applications, spanning from drug delivery systems and imaging agents to separations and reinforcing fillers in composite materials.^{1,2} The increasing demand for effective separation technologies has fuelled growing interest in the application of silica nanoparticles. These nanoparticles can be tailored to

specific requirements, allowing for the design of efficient separation materials with enhanced selectivity and capacity. For example, their surface chemistry and porosity can be altered to tailor them for a specific target molecule to be separated.^{3–5}

In the context of oil-water separation, superhydrophobic materials are commonly employed due to their strong affinity for oil compared to water, resulting in high selectivity towards oil.⁶ Superhydrophobic silica nanoparticles have been extensively investigated in various applications, but there has been limited exploration of their use in oil-water separation. Nonetheless, existing research has demonstrated the effectiveness of hydrophobic silica surfaces and composites in facilitating oil-water separation. For example, Cho et al.⁷ used hydrophobic silica nanoparticles modified by PDMS through chemical vapour deposition to effectively remove oil from oil-water mixtures by inducing oil gelation. Furthermore, Rabbani et al.⁸ demonstrated the efficacy of carbonyl iron (CI)/silica composite particles, modified with 1H,1H,2H,2H-perfluorodecyltriethoxysilane and Hexamethyldisilazane, achieving an impressive 99% separation efficiency and a sorption capacity of 4.3 g/g. Notably, Yu et al.⁹ developed a hydrophobised magnetic silica nanocomposite for oil removal from water surfaces, achieving 89.5% separation efficiency even after 20 cycles of separation. These studies underscore the effectiveness of hydrophobic silica powders in oil-water separation.

Other powdered materials like waste tyre powder, sawdust, magnetic iron-oxide, etc., have been applied for oil-water separation and displayed outstanding performance.^{10–13} Lü et al.¹⁴ employed N-(aminoethyl)-aminopropyl functionalised core-shell magnetic nanoparticles for the separation of emulsified oils, achieving good separation and maintaining high separation efficiencies after 5 separation cycles. From a sustainability standpoint, some waste materials like eggshells have been used.^{15–17} The inherent biodegradability and low-cost nature of eggshells enhance their appeal for environmentally friendly oil-water separation applications. Eggshells can easily be hydrophobised using fatty acids through a mechanochemical modification process.¹⁸ Through mechanical forces applied during milling processes, eggshells are easily transformed into

functional materials with enhanced properties. The mechanical forces facilitate the interaction between the eggshell surface and the fatty acids, resulting in the attachment of the fatty acid molecules onto the eggshell matrix. These mechanochemically modified eggshells have demonstrated potential applications in diverse fields, including oil-water separation.

This chapter delves into the preliminary work conducted using modified silica nanoparticles and hydrophobic eggshells as potential adsorbents for recovering oils from oil-water mixtures. Additionally, the chapter provides a summary of the challenges associated with applying these materials for oil-water separation in this study.

4.2. Materials and Methods

4.2.1. Materials

Chicken eggshells were recovered from a domestic household kitchen, stearic acid (95%) was purchased from Sigma Aldrich (Gillingham, UK).

4.2.2. Two-step Synthesis of Modified Silica Nanoparticles

4.2.2.1. Silica Synthesis

Silica nanoparticles were produced using a Stöber method,¹⁹ a mixture of ethanol (100 mL), TEOS (6 mL) and DI-water (10 mL) was prepared and mixed for 5 min. Afterwards, $\text{NH}_3(\text{aq})$ (28%) (10 mL) solution or NaOH (0.4 M, 1 mL) was added. After 6 h, the particles were recovered by centrifugation (6000 rpm, 10 min) and washed twice with DI-water. The washed particles were then dried in an oven (70 °C). The samples were denoted N-SNPs and A-SNPs for NaOH and NH_3 -catalysed synthesis, respectively.

4.2.2.2. Post-grafting Surface Modification of Silica Nanoparticles

1g of dried silica nanoparticles was dispersed by sonication in a mixture of 0.50 mL of silane (PTMS, OTMS, ODTMS or APTMS) and 80 mL of cyclohexane. 0.7 mmol of TFA acid was then added to the mixture to initiate the hydrolysis of the silane molecules. The hydrolysed silane molecules then condensed with the -OH groups of the silica nanoparticles. After 2 h reaction time,

the modified particles were recovered by centrifugation (6000 rpm, 15 min) and washed thrice in a slightly basic acetone. This was followed by drying particles under vacuum overnight (200 mbar, 60 °C). The samples were denoted A/N-SNPs-F, where F is a functional group of the silane used. F is C3 for PTMS, C8 for OTMS, C18 for ODTMS and NH₂ for APTMS.

4.2.3. One-pot Synthesis of Superhydrophobic Silica Particles

The Stöber procedure, as described earlier (section 4.2.2.1) was employed, with the addition of 1 mL of ODTMS before introducing the basic catalyst. In the case of NaOH, an increased amount of 2 mL was used to enhance the reaction yield. The modified silica particles were retrieved after 6 h and washed three times with acetone. Following this, they were dried under vacuum, as outlined previously. The resulting samples were labelled as N-SP-C18 or A-SP-C18, corresponding to the NaOH and NH₃-catalysed reactions, respectively.

4.2.4. Mechanochemical Synthesis of Superhydrophobic Eggshell Powder

4.2.4.1. Pre-treatment and Conversion of Eggshells to Powder Form

The retrieved chicken eggshells were immersed in a boiling water for 30 min to remove the shell lining membrane. Subsequently, they were dried under vacuum conditions (700 mbar, 120 °C). The dried eggshells were then processed into a powder form using an electric blender, and the resulting powder was sieved to isolate particles with sizes ranging between 32-40 µm. This sample was labelled as Raw-ES.

4.2.4.2. Hydrophobic Modification of Eggshell Powder

Dry eggshell powder (95 wt%) and stearic acid (5 wt%) were mixed together in a mortar. This was followed by grinding using a pestle for 5 min to enhance the attachment of fatty acid to eggshell powder. The resulting powder was washed once in ethanol to remove excess unattached stearic acid. Washed powder was then left to dry at room temperature overnight. The sample was denoted ES-SA.

4.2.5. Characterisation of the Samples

The silica nanoparticles were characterised using SEM, WCA, and TGA, as elaborated in Chapter 3. In the case of WCA, the powders were compacted into tablets to achieve a flat surface. Additionally, the particle size was determined using dynamic light scattering (DLS) in a Litesizer 500 (Anton Paar GmbH, Austria). A 2 wt% silica dispersion was sonicated in ethanol for 10 min at room temperature.²⁰ Subsequently, 2 mL of the dispersion was added into a standard volume disposal cuvette and the measurements (20 runs per measurement) were conducted with a run time of 10 s. It is important to note that only TGA and WCA characterisation techniques were utilised for the eggshell powder.

4.2.6. Oil-water Separation

0.5 g of powder was dispersed in water, which contained 0.5 mL of olive oil. After 5 min, the powder was filtered out, and the remaining oil in the water was quantified using a UV-Vis spectrometer, as detailed in Chapter 3.

4.3. Results and Discussions

4.3.1. Morphology and the Wettability of the Prepared Samples

The two-step synthesis of silica nanoparticles yielded spherical and monodispersed particles for both NaOH and NH₃-catalysed reactions (Figure 4.1a,b). Similar observations have been previously reported in the literature for Stöber method using both bases as catalysts.^{19,21} However, in the case of the one-pot synthesis for both catalysts, a deviation from the typical spherical morphology was observed (Figure 4.1c,d). This deviation was more pronounced in the NaOH-catalysed reaction mixture. The increased amount of NaOH used led to the rapid hydrolysis of both TEOS and ODTMS due to the extreme pH of the mixture, leading to the irregular assembly of the monomers. The side chains of ODTMS are also believed to influence the monomer arrangement, with the chains possibly becoming entangled within the structure, contributing to an irregular overall shape. Furthermore, the particle size of the one-pot silica particles, especially in the NaOH-

catalysed samples, was remarkably larger compared to the two-step process. The average diameter of the N-SP-C18 particles was determined to be 1184 ± 107 nm, while it was 500 ± 4 nm for A-SP-C18. Despite the presence of ODTMS silane in the reaction, the slow hydrolysis and condensation reactions, facilitated by the $\text{NH}_3(\text{aq})$ catalyst, appeared to prevent excessively large particle sizes.²² On the other hand, the two-step synthesis produced particles with sizes of 513 ± 28 nm and 371 ± 9 nm for N-SNPs and A-SNPs, respectively. Contrary to the findings of this study, spherical modified silica nanoparticles have been successfully synthesised using a one-pot approach in the literature.^{23,24} To achieve this, the modifying silane needs to be added later, after the primary particles have formed, to avoid significant alterations in the particle morphology.^{24,25}

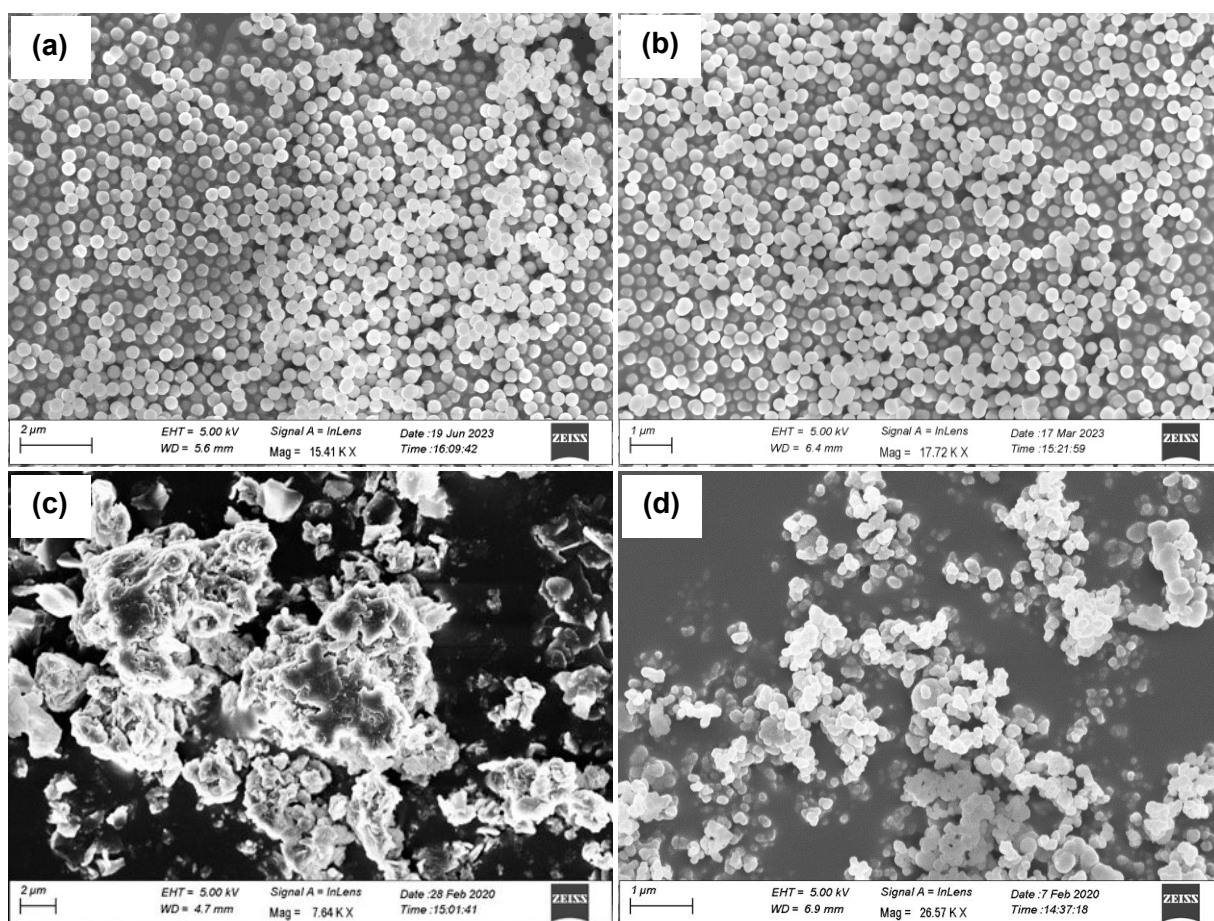


Figure 4.1 (a,b) SEM images of unmodified silica (a) N-SNPs, (b) A-SNPs. SEM images of one-pot modified silica particles (c) N-SP-C18, (d) A-SP-C18.

The wettability characteristics of the samples were assessed by measuring their WCA, as illustrated in Figure 4.2. The APTMS silane resulted in hydrophilic surfaces because of its hydrophilic terminal $-\text{NH}_2$ groups, resulting in WCAs of $83.0 \pm 1.3^\circ$ and $77.2 \pm 1.6^\circ$ for N-SNPs-

NH₂ and A-SNPs-NH₂, respectively. These WCA values were higher than those observed for unmodified samples, which exhibited highly hydrophilic surfaces with WCA values of 0°. Despite the hydrophilic nature of the APTMS silane's terminal groups, the presence of a propyl-alkyl chains decreased the overall hydrophilicity of the silica nanoparticles' surface.

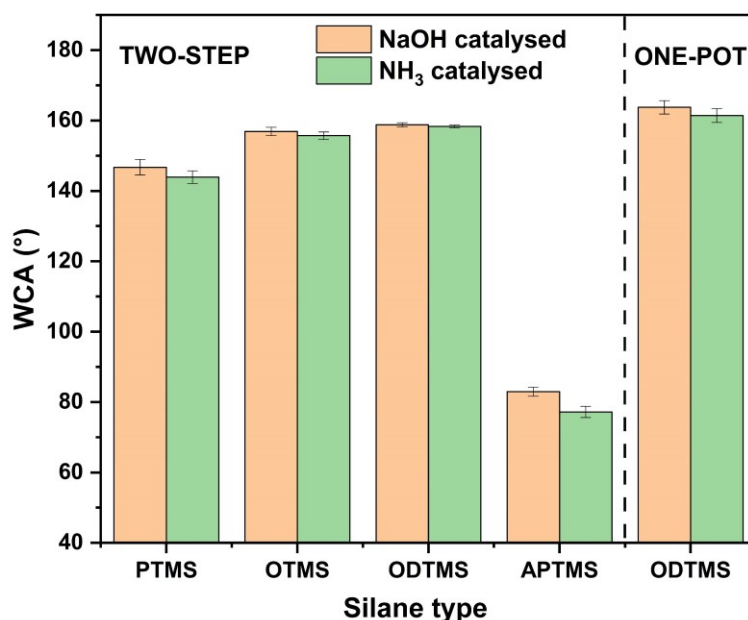


Figure 4.2 WCA of the modified silica particles functionalised by both post-grafting and one-pot methods.

The hydrophobicity introduced by the alkyl chains prevented water droplets from quickly penetrating the prepared tablet, as observed in the unmodified silica nanoparticles. For nanoparticles modified with hydrophobic silanes, the WCA was significantly higher, exceeding 140°. PTMS achieved 146.7° and 143.9° for N-SNPs and A-SNPs, respectively. OTMS and ODTMS resulted in superhydrophobic surfaces with WCAs of 156.9° and 158.8°, respectively, for N-SNPs, as well as 155.7° and 158.3°, respectively, for A-SNPs. These results indicate that WCA increases with the length of the alkyl chain of the silane's functional group, as depicted by their chemical structure in Chapter 3. WCA values were consistently slightly higher for N-SNPs compared to A-SNPs. This is attributed to the highly reactive surfaces of NaOH-catalysed silica particles.¹⁹ The one-pot synthesis method resulted in highly superhydrophobic silica particles compared to the two-step process, achieving WCAs of 163.8° and 161.4° for N-SP-C18 and A-SP-C18 samples, respectively. This is because the one-pot synthesis introduces the functional group

in-situ, allowing more incorporation of the silane molecules into the silica matrix without limitations in terms of the particle surface available for modification, as is the case for two-step process. The WCA of modified eggshell powder was also measured and determined to be 156.0° , indicating that the ES-SA exhibited a superhydrophobic surface compared to the hydrophilic raw eggshell powder (WCA = 0°).

4.3.2. Thermal Analysis

TGA analysis, conducted under an air atmosphere, was employed to evaluate the thermal properties of the prepared silica samples, and the results are presented in Figure 4.3. As shown, the thermograms of unmodified silica nanoparticles reveal two distinct weight loss regions. The first region, spanning 100 to 200 $^\circ\text{C}$, is attributed to the loss of moisture and any volatile residual solvents present in the powder samples. The second weight loss region, extending from 200 to 800 $^\circ\text{C}$, is associated with the gradual loss of silanol groups on the surface of silica nanoparticles.²⁶ In the case of NaOH-catalysed silica nanoparticles, the thermogram plateaus around 500 $^\circ\text{C}$, indicating the removal of all silanol groups.

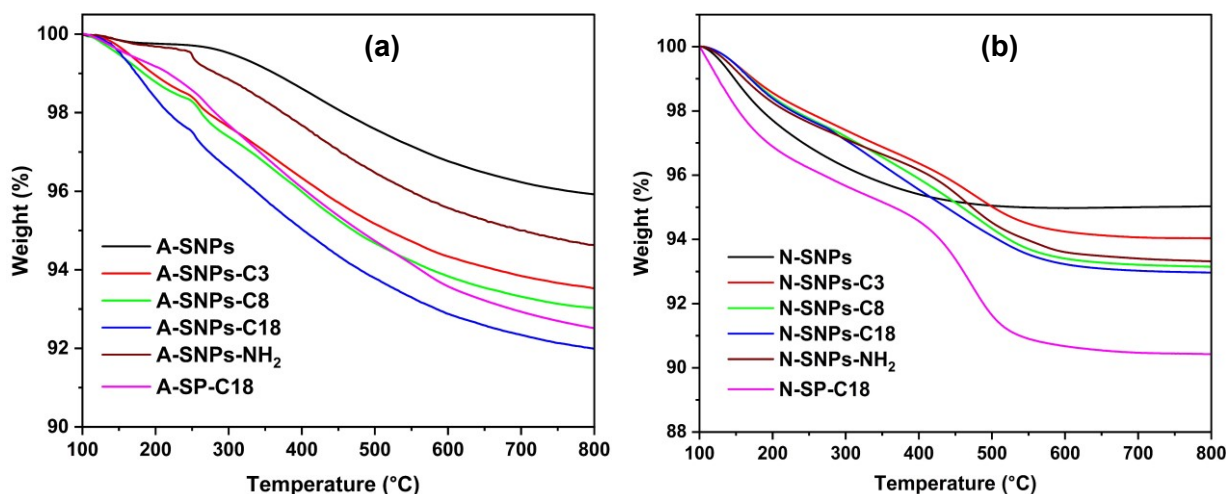


Figure 4.3 TGA curves of silica particles. (a) Silica particles from NaOH-catalysed synthesis, (b) silica particles from NH₃-catalysed synthesis.

This phenomenon has been observed previously, albeit occurring at 600 $^\circ\text{C}$ for a synthesis reaction left overnight,¹⁹ implying that the reaction time influences the quantity of silanol groups on the silica surface. For A-SNPs sample, there is a gradual weight loss observed until 800 $^\circ\text{C}$, indicating

a higher concentration of silanol groups compared to N-SNPs. The weight losses between 200 and 800 °C were determined to be 2.7% and 3.8% for N-SNPs and A-SNPs, respectively. The modified samples exhibited higher weight losses compared to unmodified samples due to the removal of the combustible functional groups deposited on the surface of particles. The decomposition of the functional groups (alkyl chains for PTMS, OTMS, ODTMS, and a combination of alkyl chains and -NH₂ groups for the APTMS) occurs after 250 °C under air.²⁶ The relative weight losses of the samples due to the removal of functional groups are summarised in Table 4.1. The one-pot synthesis method showed higher weight loss compared to the two-step method, further indicating that in the two-step method, grafting density is limited by the particle surface available for modification.

Table 4.1 Summary of the weight losses between 200-800 °C due to decomposition of functional groups.

Silane	Weight loss attributed to functional groups (%)			
	N-SNPs	N-SP	A-SNPs	A-SP
APTMS	2.3	-	1.2	-
PTMS	1.9	-	1.6	-
OTMS	2.6	-	1.9	-
ODTMS	2.8	3.8	2.5	3.0

Note: These weight losses are calculated as weight loss of the modified sample minus that of unmodified sample to determine the contribution of functional groups.

TGA analysis was also conducted for the eggshell powders, as depicted in Figure 4.4. Unmodified eggshells, mostly composed of CaCO₃ (94.0%),¹⁸ decomposed to CaO between 620 and 895 °C with a weight loss of 43.1%, releasing CO₂ and leaving a residual weight of 55.9%.²⁷ This characteristic eggshell thermogram has been reported in the literature.^{28–30} In contrast, stearic acid-modified eggshells displayed a completely different thermograph with three distinct regions. The initial region, between 200 and 420 °C with a weight loss of 17.7%, is attributed to the decomposition of stearic acid coating. The decomposition of tightly bound stearic acid molecules

due to the mechanical forces during synthesis occurs between 420 and 550 °C, resulting in an observed weight loss of 13.5%. Stearic acid has been shown to decompose between 200 to 550 °C.^{31,32} The last region observed from 660 to 835 °C, with a weight loss of 30.6%, is associated with the degradation of the CaCO₃ component of eggshells, resulting in a final residual weight of 38.2%.

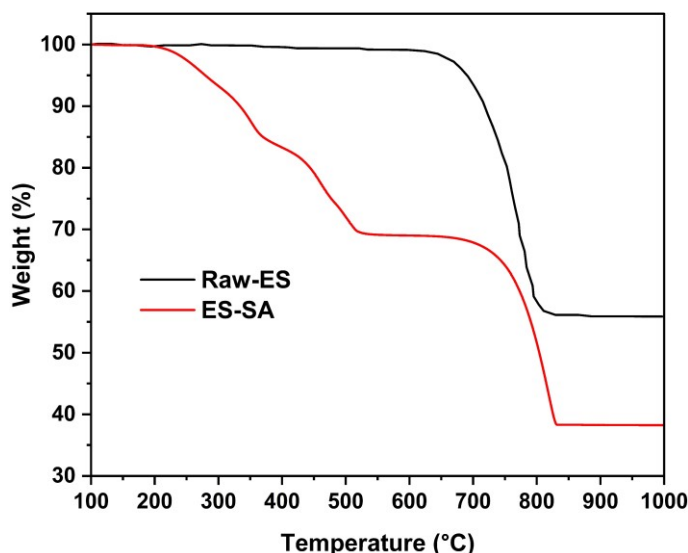


Figure 4.4 TGA curves of eggshells.

4.3.3. Application for Oil-water Separation

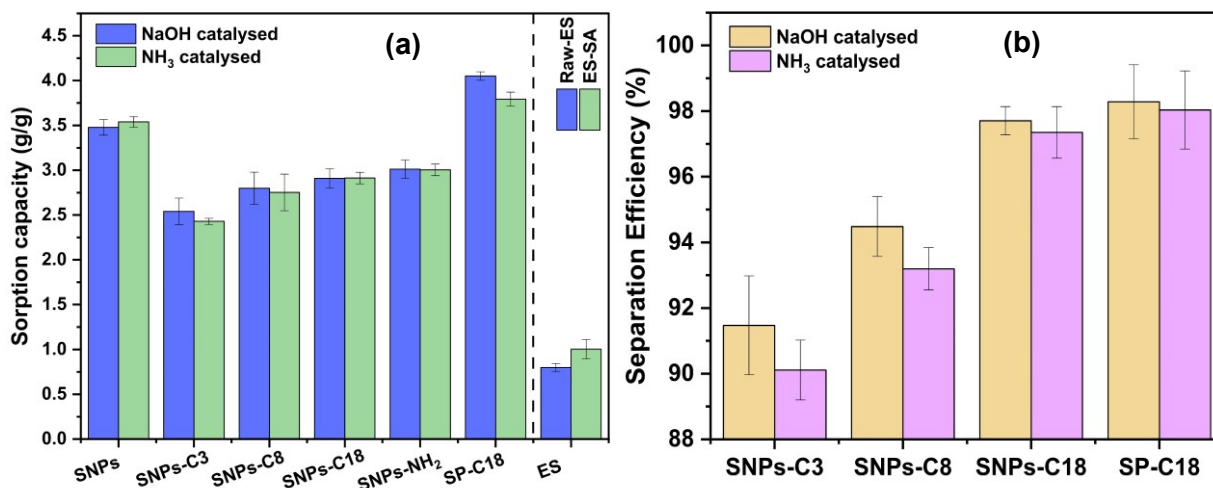


Figure 4.5 Performance testing of the powder adsorbents prepared. (a) maximum oil-sorption capacity of the powders at room temperature, (b) olive oil-water separation efficiency of the adsorbents at room temperature.

The prepared superhydrophobic powders were firstly tested for their maximum oil-sorption capacity in a pure oil system. Specifically, 0.2 g of powder was introduced into a glass vial containing pure olive oil. The mixture was subjected to shaking using an electric shaker (200 rpm)

to disperse the powder. After 1 hour, the powder was separated from the oil through centrifugation, and its oil-sorption capacity (S_{max}) was determined gravimetrically, as explained in Chapter 3. As depicted in Figure 4.5a, the oil sorption capacity of the powders exhibited a slight decrease upon modification. This reduction is attributed to the surface functionalisation of silica nanoparticles, which reduces their surface area, consequently lowering their oil-sorption compared to the unmodified samples.³³ The APTMS-modified powders demonstrated a superior sorption capacity among all powders modified using the post-grafting method. This enhanced performance can be attributed to the improved interaction of oil molecules with silica through hydrogen bonding with the amine groups, in addition to hydrophobic interactions with the propyl groups. Therefore, the surface chemistry also influences the interaction of materials with oil. Silica particles modified through the one-pot method exhibited higher oil sorption capacities, measuring 4.1 g/g and 3.8 g/g for N-SP-C18 and A-SP-C18, respectively. This can be attributed to the hydrophobic interactions between oil molecules and the highly hydrophobic particles, owing to the high loading of C₁₈ alkyl chains. As previously reported by Rabbani et al.⁸, a sorption capacity of 4.3 g/g was achieved for their hydrophobic silica composite. Hence, the results of this study are in line with existing literature. On the contrary, the superhydrophobic eggshell powder displayed a significantly lower oil-sorption capacity (1.0 g/g). This could be attributed to the lower surface area of the powder compared to silica particles. The reported surface area of eggshell powder in the literature falls within the range of 1–4 m²/g,^{34,35} which is lower compared to the typical surface area of Stöber silica particles, ranging from 10 m²/g and above.³⁶

Powders were evaluated for their effectiveness in oil-water separation, with a focus on superhydrophobic powders due to their water-repellent features, making them highly selective toward the oil phase. Hydrophilic powders, owing to their higher density (~ 2 g/cm³)^{19,37} and strong affinity to water, tend to sink into the water phase. The results of oil-water separation, illustrated in Figure 4.5b, demonstrate the efficacy of silica powders in separating oil from the water surface, achieving separation efficiencies above 90.0%. The one-pot synthesised powders, with their high

hydrophobicity, achieved superior oil-water separation efficiency (> 97.0%) compared to all other powders. Modified eggshells, on the other hand, displayed lower separation performance, attaining a separation efficiency of 85.7%.

The reusability of the powders for oil-water separation was assessed by regenerating them through washing in acetone three times and then recovering the particles via centrifugation. However, this process posed challenges for studying the powders' reusability due to the loss of some particles with the supernatant during centrifugation. The reusability study was conducted using the N-SP-C18 powder only. The separation efficiency of the powders was measured after every regeneration-sorption cycle, revealing an observed separation efficiency of 90.0% after 5 cycles.

Despite the effectiveness and good performance of the powders in oil-water separation, several challenges were encountered in this study. Firstly, the filtration-based separation of powders from the oil-water mixture was challenging due to their small sizes. Secondly, their low sorption capacities indicated the need for a large sorbent dosage. Thirdly, the transfer of powders from the weighing boat/paper to the oil-water mixture led to mass loss, as powders adhered to the boat/paper and container walls during separation. Finally, the powders created a dusty environment, posing a health hazard.

In summary, the study results highlight the effectiveness of superhydrophobic powders for oil-water separation. However, challenges in handling make their practical application difficult. Additionally, their low sorption capacities imply a significant quantity of powder would be required for industrial-scale applications, resulting in higher production costs. The difficulty in separating them from the oil-water mixture post-separation further complicates their application. To address these issues, magnetic silica powder composites can be employed to facilitate easy separation through magnetic means. While powder tableting could be considered, it reduces the available surface for separation. Despite aforementioned various approaches, the challenges of low sorption capacity and high sorbent loading during separation remain unresolved. Therefore, the in-situ

attachment of silica particles to cotton wool emerged as a preferable solution that will be explored in the next three chapters. Cotton wool, being a natural, biodegradable, inexpensive material readily available, addresses the identified challenges effectively.

4.4. Conclusions

Both post-grafting and one-pot surface modification methods were employed to successfully create hydrophobic silica surfaces for oil-water separation using hydrophobic silanes (PTMS, OTMS, and ODTMS). The resulting materials demonstrated an improving surface hydrophobicity with an increase in the alkyl side chain length of the modifier, with ODTMS yielding a remarkable WCA exceeding 158° . Additionally, superhydrophobic chicken eggshell powder (WCA = 156.0°) was produced through mechanochemical modification using stearic acid. The prepared surfaces exhibited notable oil-water separation capabilities, achieving a separation efficiency of 85.7% for eggshells and over 90% for silica-based powders. Despite their efficacy in oil-water separation, the powders pose challenges in their practical applications, including difficult recovery post-separation, low sorption capacity, high dosage requirements, and other handling issues associated with powders. Nevertheless, these materials offer an economical and straightforward solution for oil-water separation applicable in various industries.

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Chapter 5. Two-step Synthesis of Superhydrophobic Cotton for FOG Recovery from Wastewater

Abstract

FOG deposits in sewers have recently become a significant problem, causing financial strain on water companies, damaging sewer lines, and exposing the environment to dirty water through sanitary sewer overflows. Despite the proactive use of grease traps for physical oil-water separation, the issue of FOG deposits persists. This study proposes the use of adsorption-based oil-water separation, employing superhydrophobic cotton as a new alternative method. Durable superhydrophobic cotton was successfully prepared using a simple two-step sol-gel method, with ODTMS as a modifying silane. The resulting cotton demonstrated remarkable superhydrophobicity, evidenced by WCA above 154°. Additionally, it exhibited exceptional durability and stability when exposed to hot water, harsh acidic and alkaline solutions, as well as during a laundry test. Moreover, the cotton displayed excellent oil-water separation efficiency (> 98%) and maintained consistent performance throughout 20 reuse cycles, highlighting its high reusability. Furthermore, the modified cotton proved highly effective for separating oil from oil-water mixtures in a continuous flow system, achieving high separation efficiencies (> 99.0%). This innovative approach holds the potential to address the prevailing FOG deposit issues and contribute to more efficient and sustainable wastewater management practices.

5.1. Introduction

In recent years, FOGs deposits in sewers have emerged as a significant environmental concern and a major challenge for municipal wastewater management systems worldwide.^{1,2} FOGs, commonly derived from household and industrial activities, pose a substantial threat to the sewer systems and the public. As urbanisation and industrialisation continues to grow, the accumulation of FOGs in sewers has become a pressing issue that demands immediate attention. The current

methods used for FOG management as mentioned in chapter 2 have proven to be limited in their effectiveness to control FOG deposits. Therefore, it is important to develop new technologies to tackle the FOGs.

As detailed in chapter 2, superhydrophobic materials have shown to be superior in oil-water separation. However, these materials have not been sufficiently applied for FOG recovery from wastewater. Therefore, this study explores the use of superhydrophobic cotton sorbent to remove FOGs from wastewater. Superhydrophobic cotton is fabricated using a two-step sol-gel process. Firstly, wax free pre-treated cotton is loaded with silica nanoparticles using the Stöber silica synthesis method. This is followed by post synthesis surface modification using ODTMS hydrophobic silane. The surface morphology was investigated before and after modification using SEM. In addition, the wettability and the durability of prepared cotton were tested. Furthermore, the oil/fats-water separation of the modified cotton was demonstrated. The cotton displayed remarkably high oil-water separation efficiency ($> 98.0\%$) for different oil-water mixtures, even after reusing for 20 cycles. Moreover, the cotton displayed high separation efficiency ($\sim 100\%$) towards wastewater with congealed beef fats.

5.2. Materials and Methods

5.3.1. Materials

In addition to materials outlined in chapter 3, beef tallow and coconut oil were sourced from a local supermarket. Some oils/oily wastewater samples were sourced from a domestic household kitchen after grilling/cooking beef, chicken and salmon fish.

Recovered oils/oily wastewater samples were filtered to remove any solid food particles; fats were liquified before filtering.

All other chemicals and reagents were used without further purification.

5.3.2. Cotton Pre-treatment

The acetone washed cotton was etched in 1.0 M NaOH solution for 10 min as previously reported.³ Etched cotton was then recovered and washed in DI-water several times until the supernatant pH was close to neutral. Finally, it was dried at 60 °C until completely dry.

5.3.3. Synthesis of Silica-loaded Cotton

To load silica nanoparticles onto cotton wool, a mixture of ethanol (1.7 mol), DI water (0.6 mol) and TEOS (30.0 mmol) was prepared. The prepared mixture was stirred for 5 min (500 rpm, RT) using a magnetic stirrer, followed by soaking 1.0 g of pre-treated cotton in the mixture for another 5 min. Then, NH₃ solution (80.0 mmol) or NaOH (0.3 M, 1.2 mmol) was added dropwise to the mixture and the solution was left to react for 8 h. The silica loaded cotton was recovered and washed twice in ethanol. The washed cotton was then dried in an oven (80 °C) until completely dry. The dry weight gain (w) was calculated from:

$$w(\%) = \left(\frac{m_f - m_i}{m_i} \right) \cdot 100\% \quad (5.1)$$

Where m_i is the initial mass of etched cotton and m_f is the final mass of silica-loaded cotton immediately after drying. The cotton samples were denoted N-C and A-C for NaOH and NH₃ catalysts used. Two additional samples were produced using the same method but with addition of 0.56 mmol of APTMS. The samples were denoted N-C_{NH2} and A-C_{NH2}.

5.3.4. Hydrophobic Surface Modification of Silica-loaded Cotton

Silica-loaded cotton was added to ethanol (1.7 mol) with 5.3 mmol of ODTMS, followed by addition of NH₃ solution (50.0 mmol). The cotton was recovered after 7 h, washed thrice in acetone and dried in an oven (80 °C). The dried cotton was further treated with compressed air (2.0 bar). The modified samples were denoted N-C-C18 and N-C_{NH2}-C18 for NaOH catalysed silica-sol. Conversely, for NH₃ catalysed silica-sol the modified samples were labelled A-C-C18 and A-C_{NH2}-C18.

5.3.5. Batch Oil-water Separation

This investigation was carried out as outlined in chapter 3. Additionally, the impact of contact time was explored at room temperature. The modified cotton sample was added to olive oil-water mixture and left for different contact times ranging from 2 s to 1.5 min. Subsequently, the cotton samples with adsorbed oil were retrieved and weighed using a microbalance. The sorption capacity was then calculated using equation 3.10. The PFO and PSO sorption kinetic models were fitted to the contact time experimental data. More information is provided in chapter 2 about these kinetic models.

5.3.6. Continuous Oil-water Separation

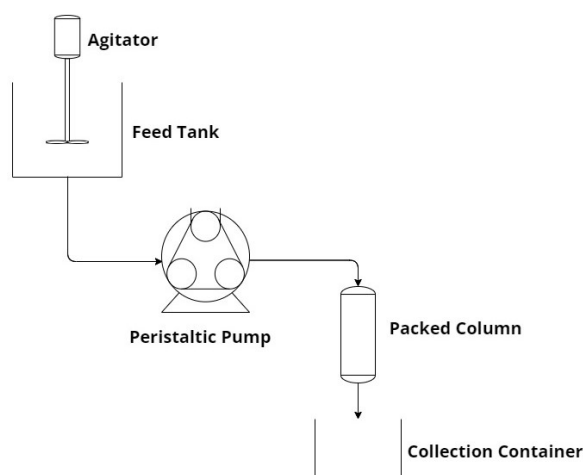


Figure 5.1 Schematic of the experimental set-up for the continuous flow separation.

1 g of modified cotton was densely packed into a column (syringe barrel) with a packing height of 4.8 cm and a column internal diameter of 1.6 cm. A piece of stainless-steel mesh was mounted as a base support in the column to avoid cotton from blocking the outlet during operation. A 500 mL oil-water mixture, with an oil concentration of 20 g/L, was prepared using tap water and olive oil. The mixture underwent vigorous mixing to disperse the oil in water, forming a homogeneous mixture. This prepared mixture was then pumped through the packed column from the top using a peristaltic pump at a rate of 10 rpm (36.7 ± 0.8 mL/min; refer to the pump calibration curve in Figure A.1 in the appendix) as depicted in Figure 5.1. Samples were collected over time and analysed using UV-Vis spectrometer after oil extraction with hexane. Separation efficiency

was calculated from:

$$E (\%) = \left(\frac{C_0 - C_e}{C_0} \right) \cdot 100\% \quad (5.2)$$

where C_0 and C_e are column feed and exit oil concentrations, respectively. The value of C_e used to calculate $E (\%)$ was determined from a sample collected at ~90% bed saturation. For simplicity, this was translated to 90% of the packed bed height and marked on the column.

5.3. Results and Discussions

5.3.1. Synthesis of Modified Cotton

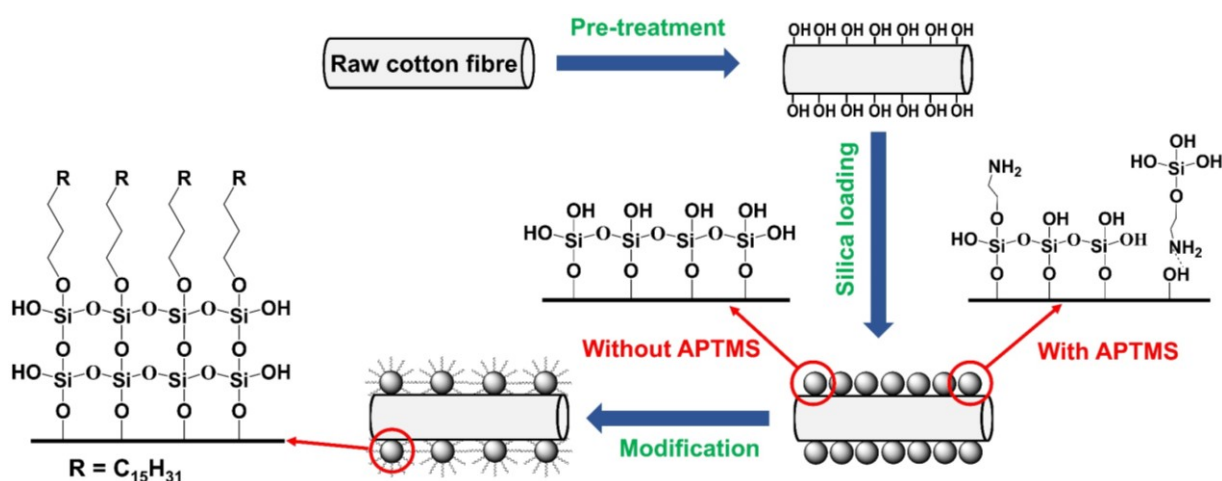


Figure 5.2 Schematic illustration of the two-step preparation process of superhydrophobic cotton.

The two-step process of creating superhydrophobic cotton wool is illustrated in Figure 5.2. The pre-treatment of raw cotton with NaOH exposes the hydroxyl groups on the fibres by removing the wax layer.⁴⁻⁷ However, it was observed that prolonged exposure to the NaOH solution led to the lumping together of cotton fibres which is undesirable. Subsequently, silica nanoparticles were attached to the cotton using the Stöber sol-gel method. The attachment is due to hydrogen bonding of hydroxyl groups of cotton with the silanol groups of silica particles and the amine groups of the APTMS.⁸ Furthermore, condensation reactions between silanol groups of silica particles and hydroxyl groups of cotton fibres may also occur, resulting in covalent bonding between silica particles and cotton fibres.⁹⁻¹¹ After washing and drying these samples, the silica-loaded cotton undergoes modification with ODTMS silane.

The silane undergoes hydrolysis using ammonia, leading to the formation of a more reactive intermediate where methoxy groups are replaced by hydroxyl groups. Subsequently, the hydroxyl groups of the silane intermediate condense with both the silanol groups and any unreacted hydroxyl groups on the cotton fibres, thereby modifying the surfaces of the cotton fibres.

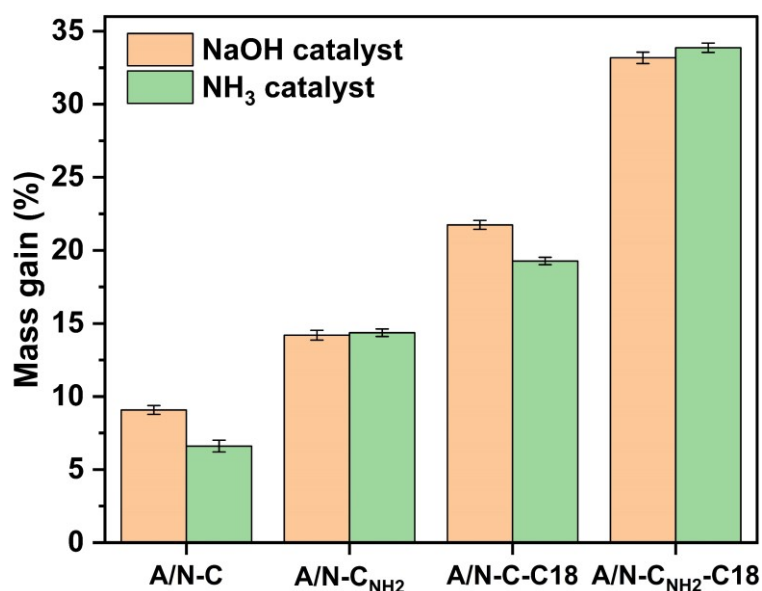


Figure 5.3 Overall mass gain of cotton wool during the two steps of preparation process.

Overall mass gain during the two steps is shown in Figure 5.3, with the first step resulting in 6.6% and 9.1% mass gain for NH₃ and NaOH-catalysed silica-sols, respectively. The addition of APTMS silane increases the mass gain to 14.4% and 14.2% for ammonia and NaOH-catalysed silica-sols. The higher mass gain of the N-C sample may be attributed to adsorbed sodium ions, enhancing attachment to cotton through electrostatic interactions.^{12,13} N-C_{NH2} and A-C_{NH2} exhibited similar mass gain, possibly due to the acidic interaction of APTMS amine groups with the bases, affecting attachment in NaOH-catalysed silica-sol. Overall, APTMS is observed to enhance silica loading onto cotton by acting as a coupling silane and bridging the attachment. Surface modification further increased the mass gain, with A/N-C_{NH2}-C18 displaying higher mass gain than A/N-C-C18 due to a higher concentration of reactive sites on unmodified samples. Overall mass gains for N-C_{NH2}-C18 and A-C_{NH2}-C18 are 33.2% and 33.9%, respectively, while N-C-C18 and A-C-C18 displayed

mass gains of 21.8% and 19.3%. In summary, the samples show significant silica loading even after treatment with compressed air, indicating a robust attachment of silica particles.

5.3.2. Morphology and the Wettability of Prepared Cotton Wool

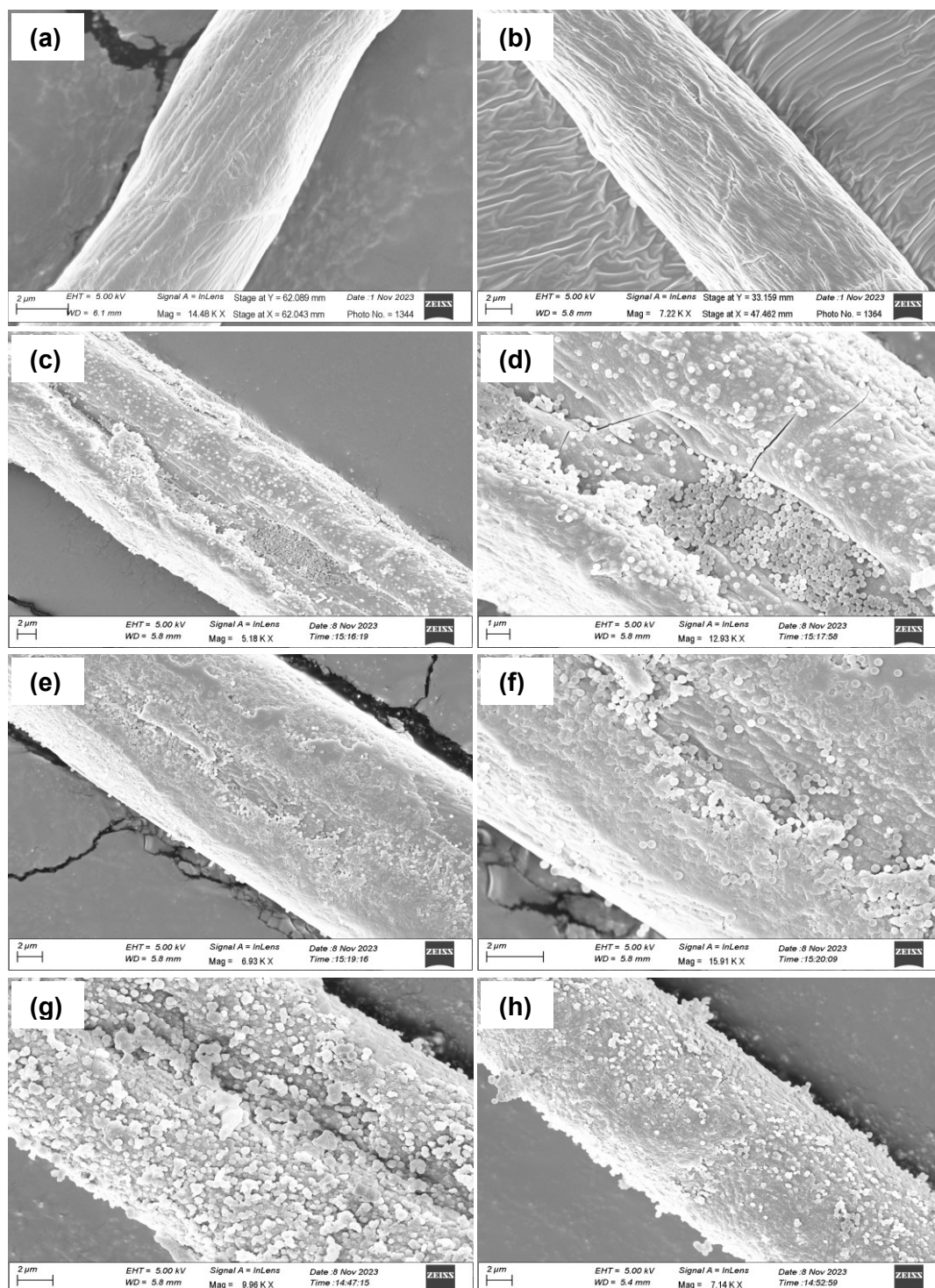


Figure 5.4 SEM images of (a) raw cotton, (b) pre-treated cotton, (c, d) A-CN_{H2} cotton sample at low and high magnification, i.e. cotton loaded with silica nanoparticles using ammonia as a catalyst, (e, f) N-CN_{H2} cotton sample at low and high magnification, from silica-sol using NaOH as a catalyst, (g, h) ODTMS modified A-CN_{H2} and N-CN_{H2} cotton samples.

SEM imaging revealed that raw cotton fibres exhibit grooves or veins on their surface, a characteristic that becomes more apparent after treatment with NaOH, signifying the removal of wax on the fibres. (Figure 5.4a,b). Spherical silica nanoparticles were observed on the cotton fibre surfaces after the silica loading step for both NaOH and NH_3 -catalysed silica-sols (Figure 5.4c-h). A significant quantity of particles was observed on each fibre, aligning with the high silica loading results observed for silica-sols with APTMS. Spherical particles were also observed for A/N-C samples (Figure A.2 in the appendix). However, upon modification (Figure 5.4g, h), the particles lost their spherical shape due to the deposition of ODTMS silane molecules. This is because ODTMS can undergo self-polymerisation into hydrophobic irregular shaped silica particles.¹⁴ The attached silica particles significantly increased the surface roughness of the cotton wool fibres, as shown by the SEM images.

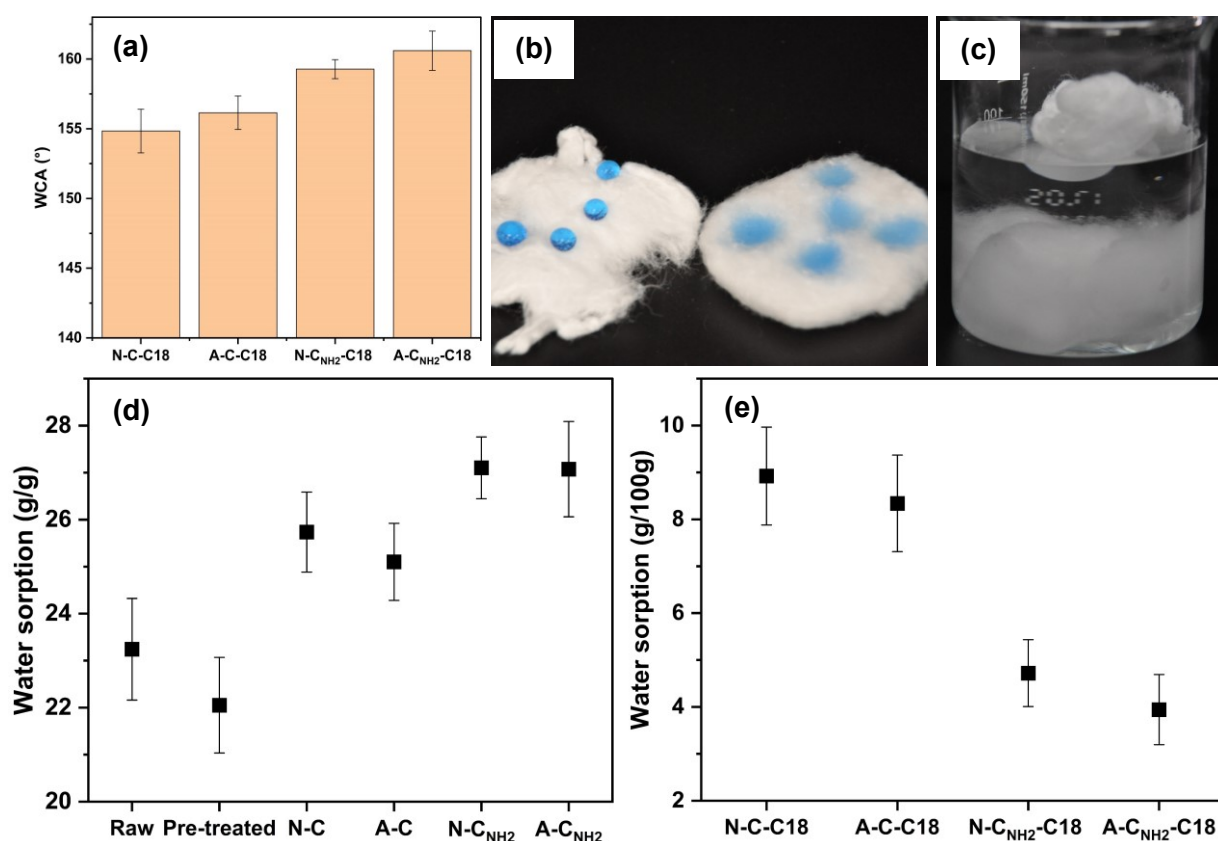


Figure 5.5 (a) WCA of modified cotton samples, (b-c) images showing the superhydrophobicity of cotton by interactions with water, (d-e) water sorption of unmodified and modified cotton samples, respectively.

The wettability features of the modified cotton were investigated by measuring the WCA and water sorption, as well as visualising interactions of water with cotton as shown in Figure 5.5. Due

to the hydrophilic nature of cotton wool and unmodified silica nanoparticles, attributable to the high concentration of hydroxyl groups, the WCA was determined to be zero for unmodified cotton samples. Water sorption also improved for the silica-loaded unmodified cotton samples, as depicted in Figure 5.5d. The N-C and A-C recorded water sorption of 25.7 and 25.1 g/g, respectively, representing a 10.7% and 8.0% increase over raw cotton. The pre-treated cotton showed slightly lower water sorption compared to raw cotton due to the fibre lumping effect caused by NaOH, which reduces the absorbency of the resulting cotton. In summary, the results imply that the loaded silica nanoparticles enhance the hydrophilicity of the cotton surface.

After modification with ODTMS, the resulting samples showed significantly low water sorption (Figure 5.5e), which was lower than 10% for all samples. N-C-C18 and A-C-C18 displayed water sorption of 8.9 and 8.3 g/100g (~ 0.1 g/g), respectively, whereas N-C_{NH2}-C18 and A-C_{NH2}-C18 displayed water sorption of 4.7 and 3.9 g/100g, respectively. This is owing to the excellent water repellent properties of the modified cotton, as evidenced by their high WCA ($> 154^\circ$), implying all samples have achieved superhydrophobicity. Due to the higher ODTMS silane loading on the A/N-C_{NH2} samples, they achieved highly superhydrophobic surfaces with a WCA of approximately 160° . The water repellent features of cotton samples were also evident when blue-dyed water droplets remained spherical on the modified cotton whereas they adsorbed on the raw cotton (Figure 5.5b). Additionally, the modified cotton floated on the water surface in a beaker, while unmodified cotton sank (Figure 5.5c). All these results confirm the successful fabrication of robust superhydrophobic cotton wool.

5.3.3. Chemical Properties of Cotton

The surface chemistry of cotton samples was investigated using XPS, as depicted in Figure 5.6a-c. Raw and pre-treated cotton samples predominantly consisted of carbon and oxygen atoms. Specifically, carbon atoms constituted 69.4 and 71.4% for raw and pre-treated samples, respectively, while oxygen atoms constituted 27.9 and 28.6% for raw and pre-treated samples, respectively. Traces of nitrogen (1.4%), silicon (0.6%) and calcium (0.7%) atoms were also

detected on the raw cotton surface, attributed to proteins, calcium and silicon inorganics found on cotton fibres.¹⁵ In the case of silica nanoparticles loaded cotton, silicon atoms were detected, along with an increased oxygen content. For instance, in the case of N-C, the oxygen atom composition was found to be 43.9%. These results further validate the attachment of silica particles to cotton. Additionally, for NaOH-catalysed sols, sodium atoms (2.4 and 1.1% for N-C and N-C_{NH2}) were identified, implying the attachment of sodium ions to silica nanoparticles and cotton.^{13,16} Traces of nitrogen atoms from the APTMS silane were also detected on the A/N-C_{NH2} samples. In the case of modified cotton, the composition of carbon atoms increased, signifying hydrophobic coating by the alkyl chains of the ODTMS silane. Moreover, insignificant amount of nitrogen atoms was observed for the A/N-C_{NH2}-C18 cotton, suggesting a thicker coating (> 10 nm) upon modification. The detected atoms and their compositions for each cotton sample are summarised in Table 5.1.

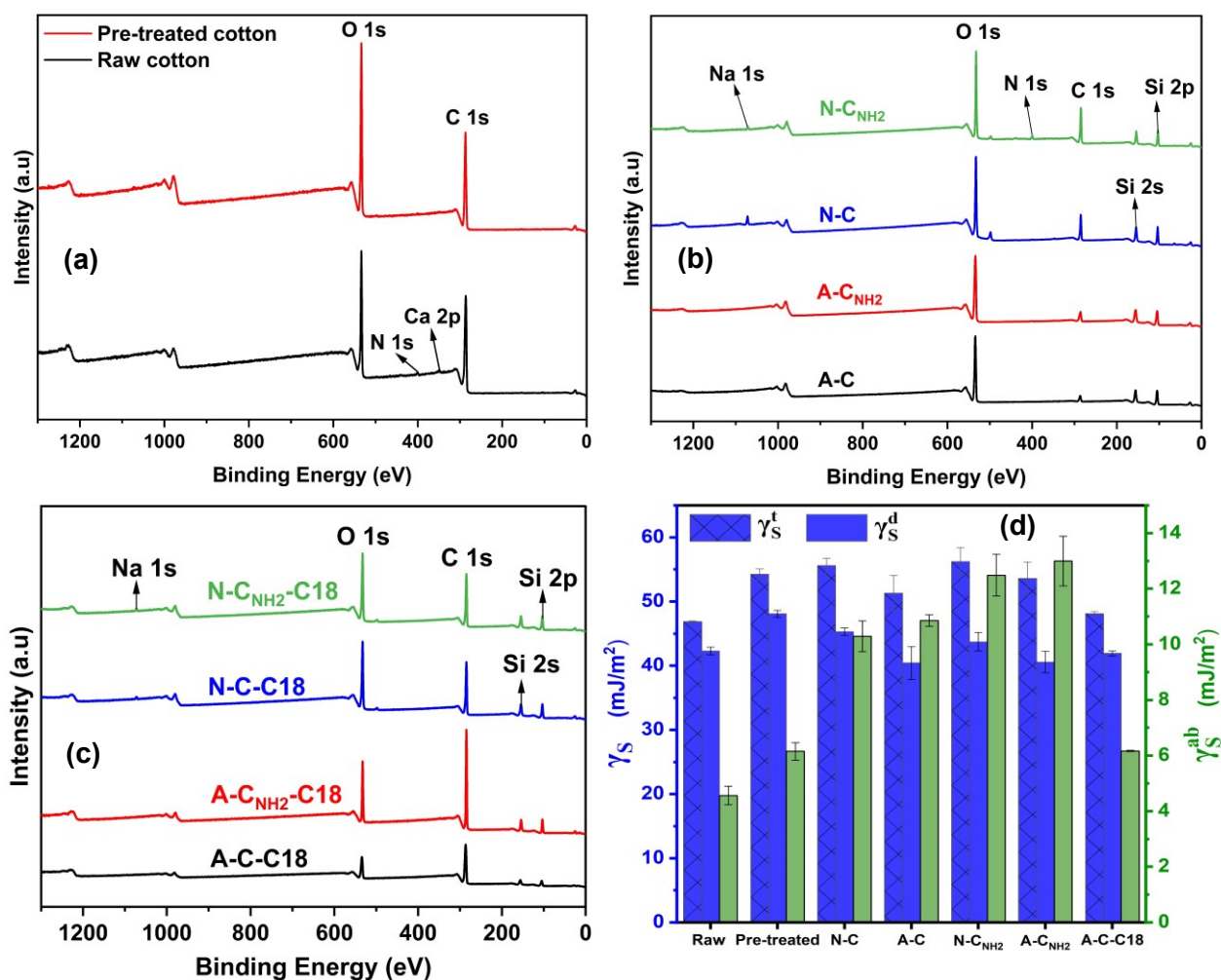


Figure 5.6 XPS survey of cotton samples, (a) raw and pre-treated cotton, (b) unmodified silica loaded cotton samples and (c) superhydrophobic cotton samples, (d) surface energy of the cotton samples at 30 °C.

Surface energy was also investigated, as shown in Figure 5.6d. Both γ_S^d and γ_S^{ab} components of surface energy for cotton slightly increased upon pre-treatment, attributed to the removal of the wax layer and other contaminants on the surface of fibres. Unmodified silica nanoparticles appeared to increase the γ_S^{ab} component of surface energy of cotton, with an increase from 6.2 mJ/m² of pre-treated sample to 10.9 and 10.3 mJ/m² for A-C and N-C cotton samples, respectively. No significant changes were observed for the γ_S^d component of surface energy, even for A-C-C18, with the values varying between 40.0-45.0 mJ/m². The γ_S^{ab} was slightly higher for the A/N-C_{NH2} samples owing to polar -NH₂ groups on the samples. The γ_S^{ab} of N-C_{NH2} and A-C_{NH2} samples was determined to be 12.5 and 13.0 mJ/m², respectively. The two samples exhibited a notable increase, higher than 6.0 mJ/m² over the pre-treated cotton, in contrast to 4.7 and 4.1 mJ/m² displayed by A-C and N-C cotton samples, respectively. For modified samples, only A-C-C18 was analysed to assess the impact of ODTMS silane on the surface energy. The results showed a decrease of 4.7 mJ/m² in γ_S^{ab} due to the hydrophobic nature of ODTMS, aligning with the fact that superhydrophobic materials have low surface energy.^{7,17}

Table 5.1 Elemental composition of cotton samples (atomic%).

Sample	C	O	N	Na	Si
N-C	31.6	43.9	-	2.4	22.1
A-C	13.9	58.1	-	-	28.0
N-C_{NH2}	40.6	38.6	3.2	1.1	16.5
A-C_{NH2}	19.4	53.7	0.9	-	26.0
N-C-C18	53.7	30.1	-	0.6	15.6
A-C-18	73.5	17.4	-	-	9.1
N-C_{NH2}-C18	53.6	30.1	0.1	0.6	15.6
A-C_{NH2}-C18	69.6	19.3	-	-	11.1

In summary, the XPS results confirm the silica loading onto cotton wool and the detected atomic compositions of the surface of the fibres. Whereas the surface energy results confirm that the silica nanoparticles increase the hydrophilicity of the cotton due to an increase in the concentration of polar groups. The results further confirm that surface hydrophobisation decreases the surface energy.

5.3.4. Durability Test of Modified Cotton

For superhydrophobic cotton employed in oil-water separation, the durability of the sorbent under varying conditions is particularly crucial. The ability of the material to maintain its superhydrophobic properties and efficient oil sorption performance over time, despite exposure to fluctuating temperatures, humidity levels, and potentially harsh chemical environments, is paramount. This durability ensures the sustained effectiveness of the superhydrophobic cotton in separating oil from water in diverse real-world scenarios, making it a reliable and practical solution for wastewater treatment applications.

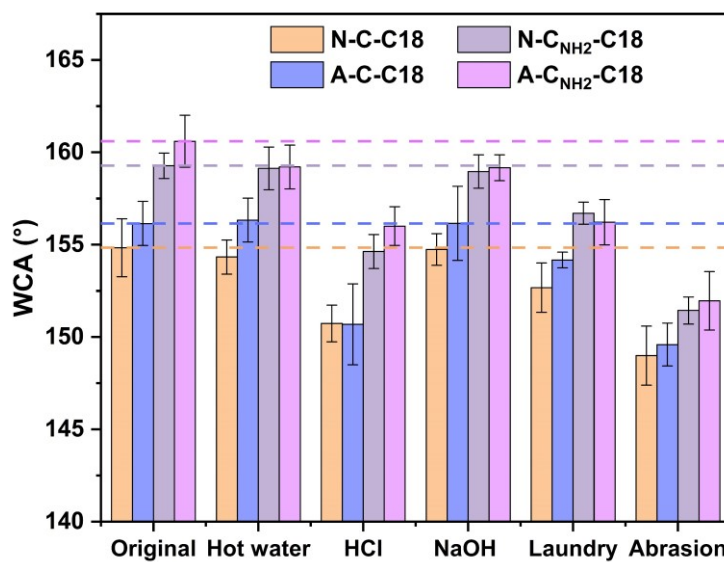


Figure 5.7 Durability studies of different superhydrophobic cotton samples.

Chemical durability was assessed by immersing cotton samples in hot water, HCl (pH = 2), and NaOH (pH = 13) solutions for 24 h and measuring the WCA. As shown in Figure 5.7, the WCA significantly dropped for the HCl solution for all samples, with a decrease of 4.1° for N-C-C18, 5.5° for A-C-C18, 4.7° and 4.6° for N-C_{NH2}-C18 and A-C_{NH2}-C18, respectively. However,

the samples still maintained their superhydrophobicity ($\text{WCA} > 150^\circ$). These changes may be attributed to the H^+ ions attached to cotton, affecting the spreading of water droplets on the cotton surface rather than damaging the coating layer. No significant decrease due to hot water and NaOH was observed, with samples displaying a slight decrease of less than 1.5° . The observed WCA changes in NaOH are expected as the synthesis already occurs under basic conditions, indicating the superior chemical durability of the modified cotton samples.

The laundry test was conducted to assess the durability of superhydrophobic cotton in detergent solutions. Understanding the material's resilience to detergent exposure ensures its sustained effectiveness in real-world applications, particularly in scenarios where frequent washing may be necessary, such as in reusable oil-absorbing materials. WCAs were determined after 24 h of exposure of the modified cotton samples to detergent. As indicated by the results, N-C-C18, A-C-C18, and N- C_{NH_2} -C18 displayed a WCA decrease of less than 2.6° , whereas A- C_{NH_2} -C18 displayed a decrease of 4.4° . In conclusion, the samples displayed high durability to laundry conditions used. Significant reduction in WCA was observed after mechanical durability testing using abrasion, with samples showing more than a 6.0° reduction in WCA. A/N-C modified cotton samples lost their superhydrophobic surfaces, whereas A/N- C_{NH_2} -C18 samples maintained their superhydrophobicity. The heating effect due to abrasion easily disturbs the silica coating. However, it appears the effect is slower when APTMS is used to enhance the silica attachment to cotton. In summary, the created cotton exhibited remarkable durability in the face of diverse challenging conditions, all the while retaining its superhydrophobic characteristics.

5.3.5. Batch Oil-water Separation

Superhydrophobic materials have gained significant attention and widespread use in the field of oil-water separation.⁷ These materials, designed to exhibit extreme water repellence, create a unique surface that repels water while allowing oils to adhere. Herein, the oleophilicity of the prepared superhydrophobic cotton was investigated. Oil-water separation was examined using various cooking oils, fats, and recovered kitchen oily wastewaters, which simulate sources of FOGs

from domestic places and the food industry. Initially, the maximum oil sorption capacity of olive oil and recovered salmon oil was determined for different modified cotton samples to discern any differences between them.

As depicted in Figure 5.8a, the cotton samples exhibited similar sorption capacities for the same oil, indicated by the overlap in error bars. However, for the two test oils used, the A/N-C_{NH2}-C18 samples displayed slightly lower sorption capacities (~39.5 g/g for olive oil and ~41.0 g/g for salmon oil) compared to A/N-C-C18, despite their higher superhydrophobicity. This discrepancy is attributed to the higher loading of silica nanoparticles onto fibre surfaces, reducing interstitial spaces between fibres and thus diminishing cotton absorbency.

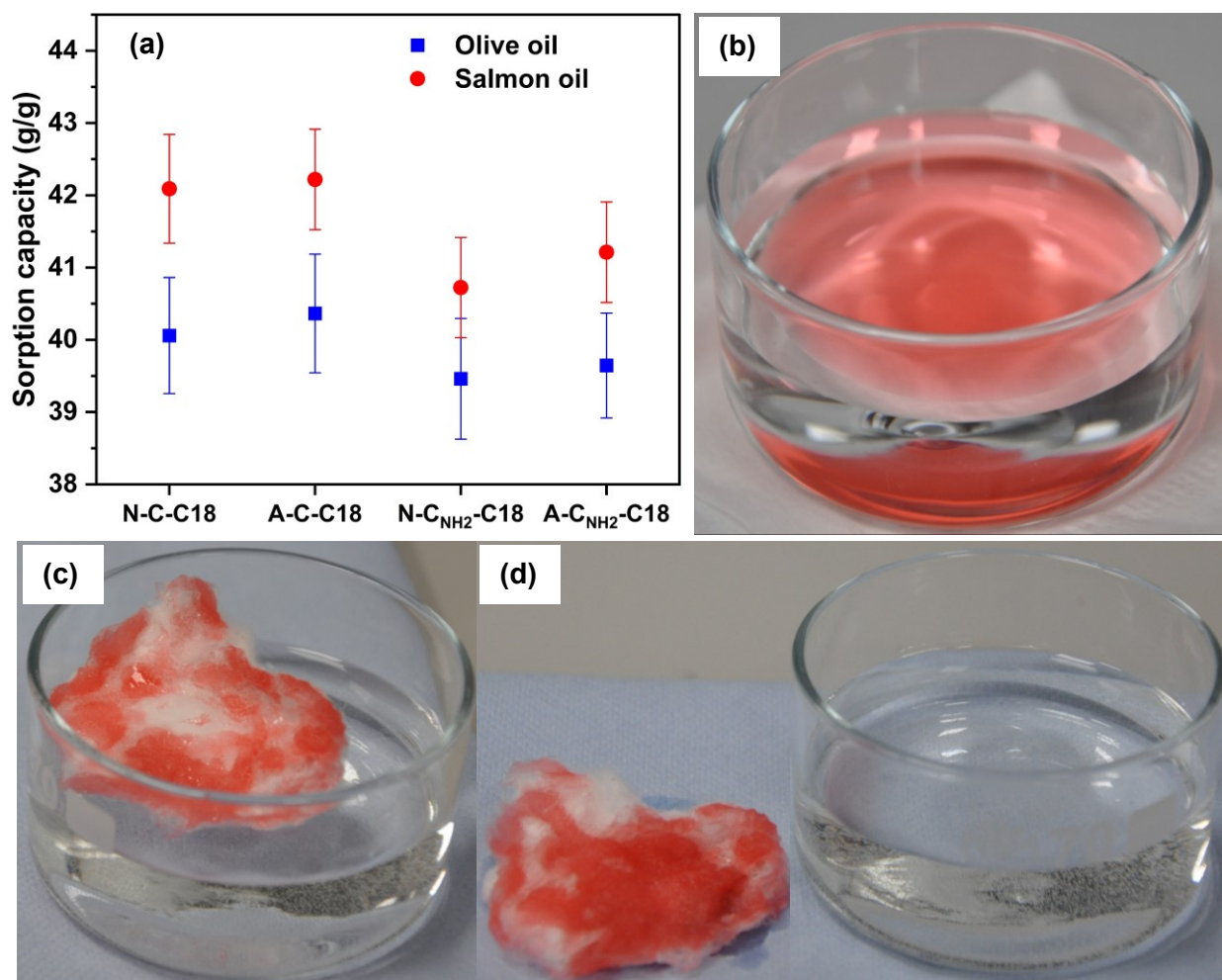


Figure 5.8 (a) Sorption capacity of olive and salmon oils on different modified cotton samples, (b-d) images visualising oil removal from water surface.

The higher sorption capacity of recovered salmon oil into cotton is attributed to the higher viscosity

of the oil compared to olive oil. The sorption capacities of the modified cotton wool are significantly higher (> 9.6 -fold) compared to the powders used in chapter 4. This implies a lower sorbent dosage for the same oily wastewater for cotton, which is practically important, as well as easier removal of the sorbent from oil-water mixtures.

Based on the results of the maximum sorption, only one cotton sample was selected for oil-water separation. From the WCA and water sorption results (Figure 5.5), the cotton samples displayed highly superhydrophobic surfaces, indicating high selectivity towards oil over water. This suggests that their separation performance will be similar since their maximum sorption capacities are comparable for the same oil. The A-C-C18 sample was chosen for oil-water separation studies. From an environmental sustainability standpoint, the process without APTMS uses fewer chemicals, resulting in a lower carbon footprint compared to the synthesis of A/N-C_{NH2}-C18. A-C-C18 is slightly more superhydrophobic than N-C-C18 and performed better in durability tests, hence its selection over N-C-C18.

The images visualising oil-water separation are shown in Figure 5.8b-d, where 2 mL of olive oil was dyed with Oil Red O before being added to the water. As shown, the modified cotton completely removed all the oil from the water surface, leaving cleaner water and demonstrating high oleophilicity. The separation efficiency for different oils was also quantified, as depicted in Figure 5.9. Modified cotton displayed separation efficiencies above 98.7% for all different oils, with the lowest separation efficiency observed for coconut oil at 98.8%. Coconut oil, beef tallow, and recovered oily wastewater from cooking beef were heated (~ 30 , 45 and 35°C , respectively) to melt the fats for easier sorption into cotton. Congealed and solidified fats are easier to separate from the water by simple filtration. The images in Figure A.3 (appendix) were taken before and after filtration of water with solidified beef-tallow using unmodified cotton wool. As shown, it was easier to filter out the fats from water, and there were no residual fats detected in the filtrate when using a UV-Vis spectrometer. This is the reason why the study primarily focuses more on oils than fats because as long as fat lumps are not broken into nano-sized particles, they can easily be

removed by filtration.

In addition to separation efficiency, the maximum oil sorption capacities of different oils into the A-C-C18 cotton were determined. As shown, the melted animal fats and oils together with coconut oil gave higher sorption capacities (> 40.0 g/g) compared to cooking oils, with the lowest sorption capacity observed for sunflower oil (35.9 g/g). This is because fats have a high concentration of unsaturated fatty acids, making them highly viscous even in their melted state compared to cooking oils. However, their viscosity will decrease as the temperature is increased, which may decrease their sorption capacity. In summary, the A-C-C18 cotton exhibited remarkable oil-water separation performance for various oils and oily wastewaters, making it versatile for industrial applications.

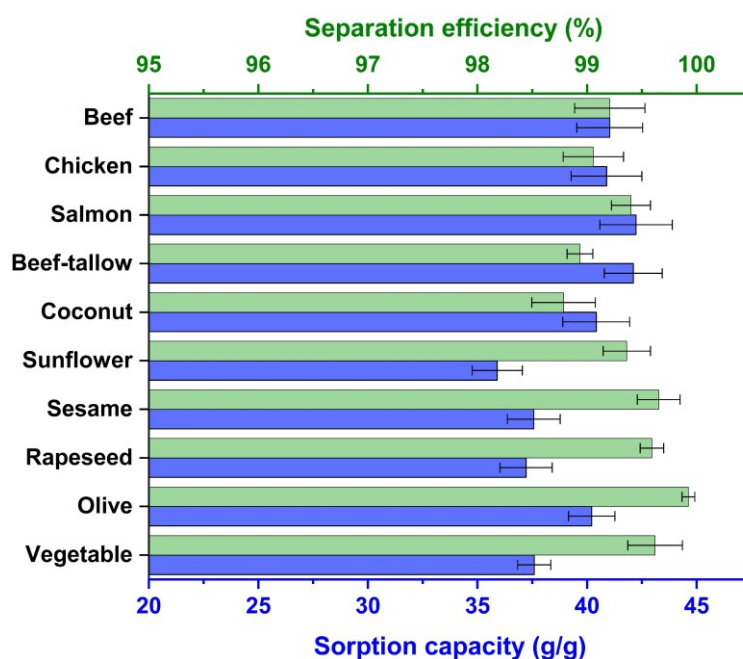


Figure 5.9 Maximum sorption capacity and separation performance of A-C-C18 cotton in a batch system.

5.3.5.1. Effects of Operational Conditions

Investigating the effects of oil-water separation conditions, including temperature and mixing rate, is crucial for optimising the efficiency of separation methods. By understanding how these factors impact the process, the speed and completeness of separation can be enhanced, leading to more effective outcomes. This knowledge is also essential for minimising energy consumption,

adapting separation techniques to different environments, and ensuring compatibility with diverse applications. In this study, the effects of contact time, temperature, and mixing rate were explored using olive oil (Figure 5.10). In the contact time study (Figure 5.10a), the sorption capacity was investigated gravimetrically using two adsorbent dosages. The dosage of 26.6 mg of cotton per gram of oil was lower than required to soak all the oil, resulting in the cotton becoming saturated after 10 s. Conversely, the dosage of 40.0 mg of cotton per gram of oil was higher than needed to remove all the oil, keeping the cotton from saturating and creating a plateau at a lower sorption capacity. The results revealed that oil sorption is a rapid process, with equilibrium for each dosage reached in approximately 10 s.

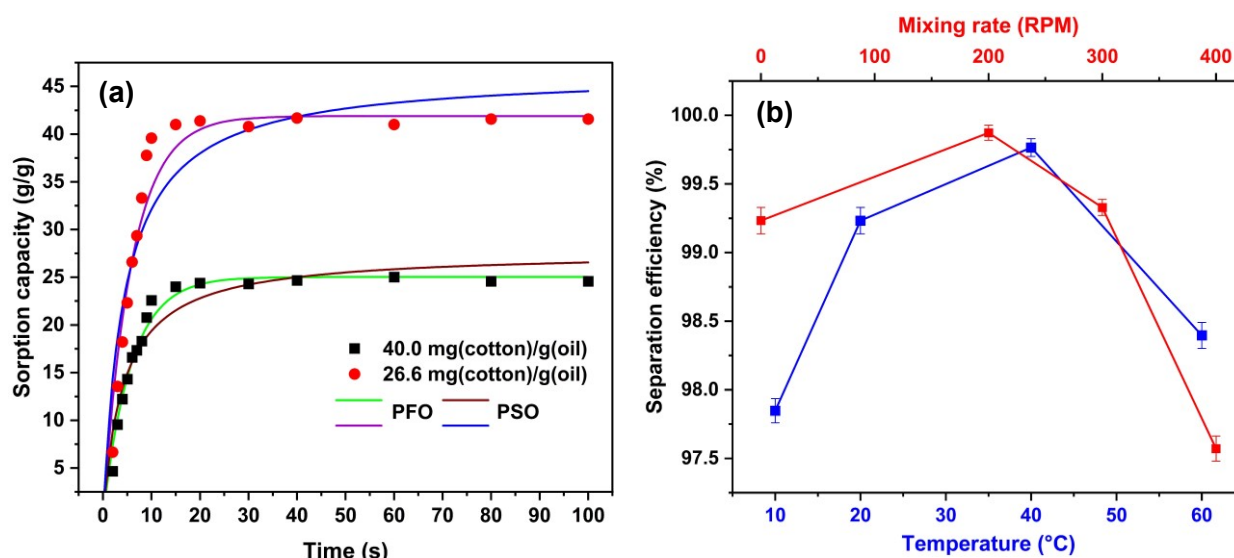


Figure 5.10 (a) effects of contact time on sorption capacity of modified cotton, (b) effects on temperature, with no mixing, and mixing rate at room temperature on separation efficiency of modified cotton in a batch system.

The experimental results were utilised to estimate kinetic parameters using two commonly employed kinetic models,¹⁸ pseudo first (PFO) and second order (PSO) kinetic models. The PFO kinetic model provided a better fit with R^2 of 0.995 and 0.998 for the dosages of 26.6 and 40.0 mg (cotton)/g (oil), respectively. In contrast, the PSO model fits poorly especially for the 26.6 mg (cotton)/g (oil) cotton dosage with Root Mean Square Error (RMSE) of 3.94 and R^2 of 0.987. In comparison, the PSO fit was relatively satisfactory for the cotton dosage of 40.0 mg (cotton)/g (oil), yielding an RMSE of 2.43 and an R^2 value of 0.992. The model parameters are summarised in

Table 5.2. The PFO model assumes that the rate of sorption depends solely on the concentration of oil, not water, and that the limiting step is the mass transfer/diffusion of oil into the cotton.¹⁹ This holds true for the oil-water mixtures in this study because they are immiscible, and the cotton does not interact with water. Due to the immiscibility of oil and water, there is no bulk diffusion of the adsorbate (oil) from the water phase to the interface, but only across the water surface, making the sorption process extremely rapid. PFO is commonly employed to describe physisorption, while PSO describes chemisorption processes.²⁰ The sorption of oil to cotton is a physisorption process involving hydrophobic interactions between the alkyl chains of free fatty acids or triglycerides in oil and those grafted on the cotton wool. Similar rapid sorption of oil to cotton has been reported in previous studies.¹⁷

Table 5.2 Values of the kinetic model parameters for the sorption of olive oil into modified cotton wool at room temperature.

Dosage [mg (cotton)/g (oil)]	PFO				PSO			
	K_1 ($\times 10^{-2} \text{ s}^{-1}$)	q_e (g/g)	RMSE ($\times 10^{-1}$)	R^2 (%)	K_2 ($\times 10^{-2} \text{ s}^{-1}$)	q_e (g/g)	RMSE ($\times 10^{-1}$)	R^2 (%)
26.6	17.0	42.0	24.4	99.5	0.5	46.5	39.4	98.7
40.0	17.3	25.0	9.6	99.8	0.8	27.7	18.2	99.2

Following the contact time study, the separation time for the investigation of temperature and mixing was adjusted to 7 s compared to the 5 min used in the batch separation studies. This adjustment allows for notable changes in the experiments. Temperature changes were investigated in a stagnant system, and the mixing study was conducted at room temperature ($\sim 23^\circ \text{C}$). As shown in Figure 5.10b, increasing temperature from 10 to 40°C and mixing rate from 0 to 200 rpm raised the separation efficiency from 97.9% (temperature) and 99.2% (mixing rate) to over 99.8%. This improvement occurs because both changes enhance the mass transfer of oil molecules into the cotton. An increase in temperature decreases the viscosity of the oil, making its flowability easier,²¹ while increasing the mixing rate enhances the collision rate of oil with cotton.⁷ However, increasing

the temperature from 40 to 60 °C and the mixing rate from 200 to 400 rpm led to a decrease in separation efficiency to 98.4% for temperature and 97.6% for the mixing rate. The lower viscosity of olive oil at 60 °C implies that it will easily drip off from the cotton when removed from the oil-water mixture, i.e. hydrophobic interactions between oil and cotton are reduced,⁷ resulting in a decrease in separation efficiency. Additionally, at higher mixing rates, the oil layer begins to break into droplets and gets dispersed into the water phase, making separation difficult. In conclusion, under the tested conditions, the modified cotton performed well, achieving separation efficiencies exceeding 97.0% at 400 rpm and 60 °C. This suggests that the cotton can function effectively in agitated or hot oily-wastewater conditions. However, under a combination of both conditions (60 °C and 400 rpm), the separation efficiency was observed to significantly drop to 89.6%.

5.3.5.2. Regeneration and Reusability of Cotton Sorbents

The easier regeneration of adsorbents and their reusability are pivotal aspects in adsorption processes.²² This not only contributes to cost-effectiveness by extending the lifespan of adsorbent materials, minimising the need for frequent replacement and new procurement, but also aligns with sustainable practices, reducing overall waste and lessening the environmental impact of the process.^{23,24} Therefore, it is imperative to investigate the efficiency of different regeneration methods and the reusability of the modified cotton sorbent. Regeneration was conducted by washing oil-soaked cotton wool with ethanol, hexane, acetone, and detergent solution. The procedure involved initially squeezing out the oil to reduce the adsorbed oil, subsequently decreasing the amount of solvent required for washing off the remaining oil. Another solvent-free method involved oil desorption onto the tissue paper; the oil-soaked cotton was wrapped with tissue paper and left for 3 h, with oil transferred from the cotton to the tissue paper through diffusion. As illustrated in Figure 5.11a, squeezing alone removed nearly 70.0% of the oil on a saturated cotton. Subsequent washing with ethanol, acetone, and hexane removed over 90.0% of the oil, with hexane reaching an impressive 99.3% removal. Remarkably, the modified cotton maintained a separation efficiency above 98.0% even after 20 separation cycles (Figure 5.11b). This underscores the

robustness of the regeneration methods employed and the sustained reusability of the cotton sorbent.

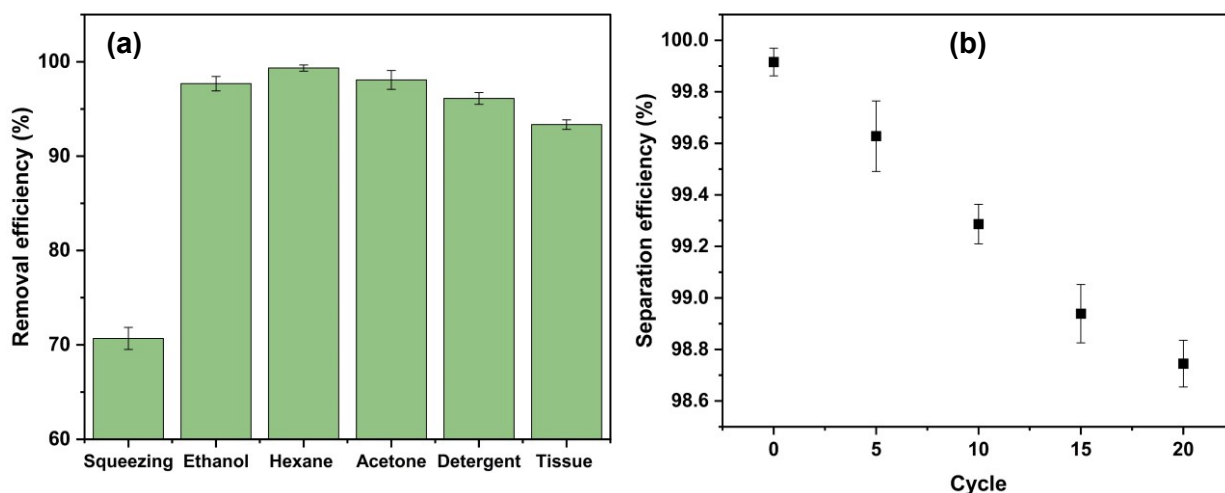


Figure 5.11 (a) Room temperature regeneration of oil-soaked cotton using different methods, (b) reusability study of modified cotton over 20 separation cycles.

5.3.6. Proof of Concept for Continuous Oil-water Separation

Continuous oil-water separation stands out as a superior choice over batch processes in industrial applications due to its ability to ensure consistent production, increased throughput, and resource optimisation.²⁵ The uninterrupted flow in continuous systems allows for better utilisation of equipment, resulting in higher processing capacities and improved efficiency. Additionally, continuous systems often occupy less physical space, are more energy-efficient, and require less manual intervention, contributing to reduced operational costs and improved safety.^{25–27} The mixed oil-water mixture was pumped through the packed column from top to bottom; however, it is worth noting that the bottom feed is desirable to prevent channelling in the column.²⁸ Consequently, the results of this study may be underestimated due to the effects of oil channelling. The high viscosity and low density of oil may lead to slow separation into two layers during operation and using bottom feed in this case could overestimate the results due to the slow flow of oil layer and gravity effects.

The photographs in Figure 5.12 show the ongoing process of oil-water separation at various stages. Figure 5.12b displays the initial phase of operation, capturing the moment when cotton begins to adsorb oil. In Figure 5.12c, the later stage is observed, where a significant portion of the

packed column height has been utilised.

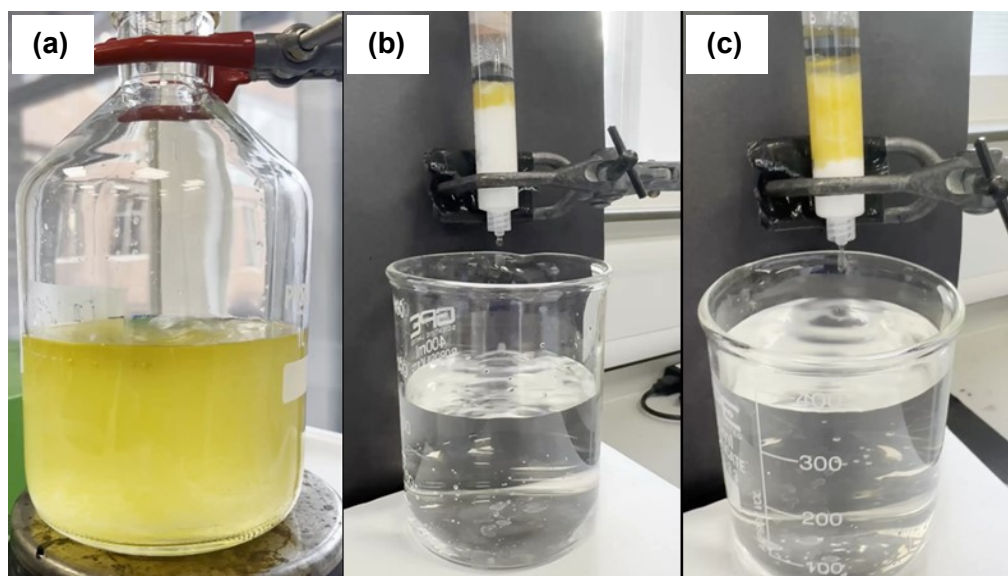


Figure 5.12 The images showing the continuous oil-water separation at different stages (a) preparation of high oil concentration feed mixture, (b) initial stage of separation where packed cotton started adsorbing oil, (c) later stage where over half of the packing height is used up.

The breakthrough curves, illustrating the dynamic behaviour of adsorption over time for two different feed concentrations (C_0), are depicted in Figure 5.13. As illustrated, the breakthrough time taken at $C_t/C_0 = 0.05$, decreases with an increase in feed concentration. Breakthrough times of 3.8 and 8.3 min were observed for feed concentrations of 20 and 10 g/L, respectively. This decrease in breakthrough time with an increase in concentration is a consequence of the saturation kinetics governing the adsorption process. Higher concentrations result in a rapid saturation of available sorption sites on the adsorbent material, as more molecules are introduced into the column.²⁸ Additionally, increased driving force and improved mass transfer for adsorption accelerate the rate at which the sites become occupied.^{28,29} The curves also indicate a steep region between the breakthrough point and bed saturation point, implying rapid saturation of the bed after the breakthrough point (2.0 and 2.1 min for 10 and 20 g/L feed concentrations). Due to the superhydrophobic nature of the cotton sorbent, it was observed that the column breakthrough point was reached only after over 90% of the packed bed height was saturated with oil. The lack of competition between water and oil molecules for adsorption sites on the cotton contributes to this observation.

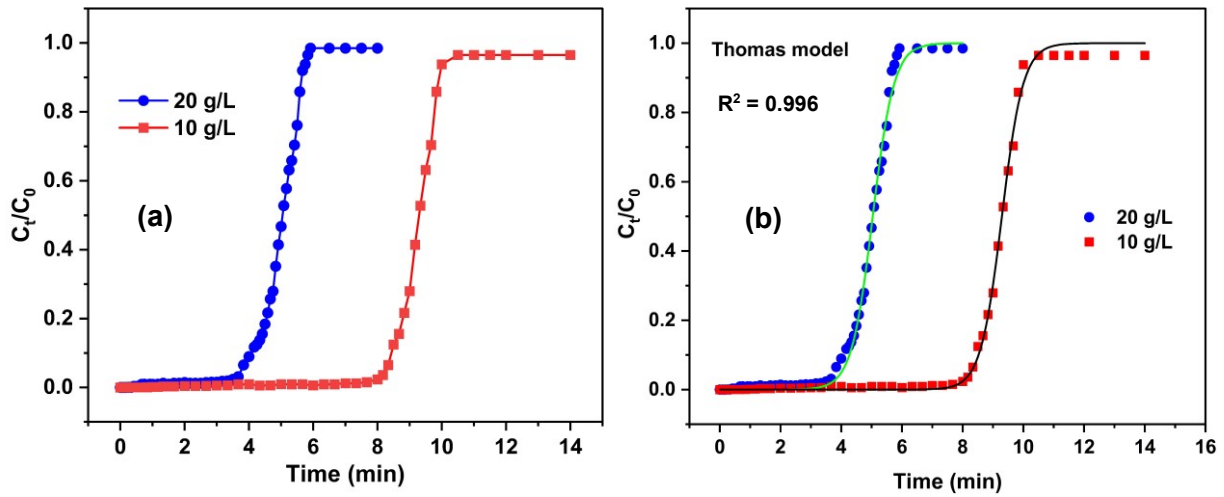


Figure 5.13 (a) Breakthrough curves of oil in packed column for 10 and 20 g/L oil feed concentrations, (b) breakthrough curve experimental data fitted with Thomas model.

Two breakthrough models, Thomas and Yoon-Nelson models were fitted to the data to obtain dynamic parameters governing oil removal. Figure 5.13b displays the nonlinear fit of the data with the Thomas model, which fits the data very well with calculated percentage R^2 of 99.6. An identical fit was obtained with the Yoon-Nelson model, as the two models are mathematically similar, as indicated by the obtained R^2 in Table 5.3.^{30–32} The model fit parameters at different feed concentrations are summarised in Table 5.3. As concentration increased, K_{TH} decreased, and q_e increased, indicating the concentration gradient's role as the driving force for oil removal in a packed column. These results align with other previous studies employing this model for dye removal.^{33,34} For the Yoon-Nelson model, K_{YN} slightly decreased, and the time (τ) needed for 50% (C_t/C_0) oil breakthrough decreased with an increase in concentration. The predicted τ values

Table 5.3 Values of the breakthrough model parameters for the continuous separation of olive oil from oil-water mixture.

C_0 (g/L)	Thomas model			Yoon-Nelson model			
	K_{TH}	q_e	RMSE	K_{YN}	τ	τ_E	RMSE
	($\times 10^{-2}$ mL/mg.min)	(g/g)	($\times 10^{-2}$)	($\times 10^{-2}$ min $^{-1}$)	(min)	(min)	($\times 10^{-2}$)
10	28.6	3.5	1.7	286.1	9.3	9.4	1.7
20	14.3	3.7	2.3	285.6	5.0	5.1	2.3

closely matched those obtained from the experimental data (τ_E), further confirming that the models effectively represent the column breakthrough data. In summary, the comprehensive investigation of continuous oil-water separation, using advanced models and breakthrough curves, not only sheds light on the dynamic parameters governing the process but also provides valuable insights into the efficiency and potential applications of such systems.

Additional investigations were conducted to determine the treated water volume under varying feed concentrations and flowrates. The experiment ended when the column was on the brink of saturation, at which point a sample is collected for separation efficiency determination using a UV-Vis spectrometer. As illustrated in Figure 5.14, all collected samples exhibited impressive separation efficiencies exceeding 99.0%. This robust performance aligns with the steep breakthrough curves observed, emphasising that oil can only reach the effluent when the entire packed column is nearly saturated. Moreover, the results indicate a decrease in the treated water volume with increasing concentrations and flowrates. Since there is no competition between water and oil for adsorption and the mass of cotton used (the sorption capacity available for oil) is constant, the amount of oil adsorbed will be consistent regardless of the feed concentrations.

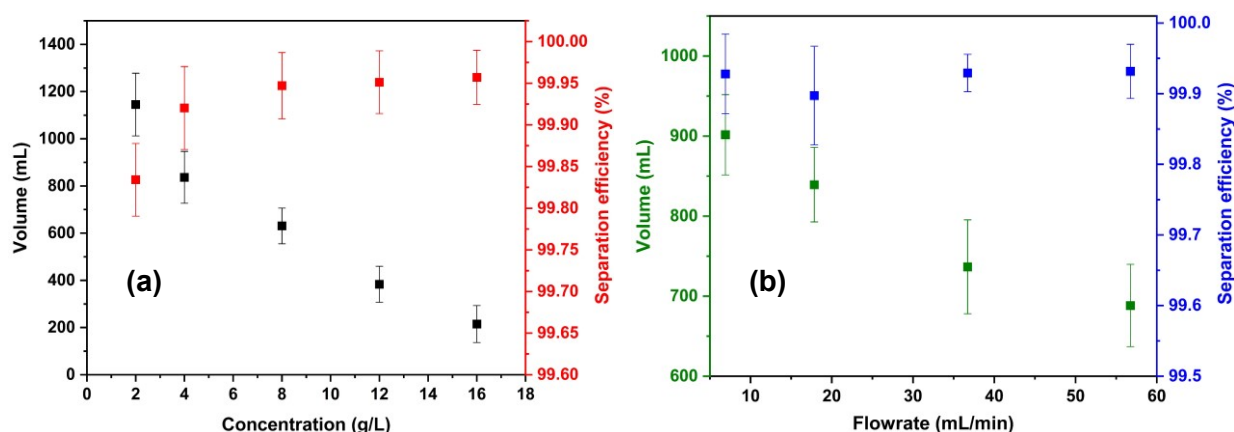


Figure 5.14 Effects of feed oil-water mixture concentration (a) and feed flowrate (b) on the volume of water treated at bed saturation point and the achieved separation efficiency.

Any minor variations in adsorbed oil may be attributed to different channelling behaviours that occur during operations. Notably, the impact of flowrates is found to be insignificant. Despite the decrease in residence time associated with elevated flowrates, the rate of oil sorption into cotton

appears to improve, mitigating the impacts of the reduced residence time. In conclusion, the results unequivocally demonstrate the viability of a continuous oil-water separation process, showcasing its optimal efficiency. These findings not only underscore the practicality of such a system but also have the potential to revolutionise oil-water separation practices within the industry, paving the way for enhanced environmental sustainability and operational effectiveness.

5.4. Conclusions

A robust superhydrophobic cotton sorbent, exhibiting exceptional oil-water separation performance, was successfully synthesised through a two-step sol-gel method. In this process, ODTMS was employed as a hydrophobic modifying silane, following the loading of silica nanoparticles onto cotton using the Stöber method. The resultant cotton samples displayed a remarkable WCAs exceeding 154° and minimal water sorption (< 0.1 g/g), confirming its superhydrophobic nature. This specially prepared cotton exhibited impressive resistance to hot water, laundry test, abrasion, and exposure to extreme acidic and alkaline solutions when immersed. The high oleophilicity of the superhydrophobic cotton facilitated the successful separation of oil from various oil-water mixtures, achieving separation efficiencies surpassing 98.0%. Additionally, the fabricated cotton proved highly reusable, maintaining similar separation efficiency even after 20 separation cycles. Furthermore, the cotton sorbent demonstrated its effectiveness in removing oils from a continuous flow of oil-water mixtures in a packed column. The combination of high-water repellence, excellent durability, remarkable oil-water separation performance, and reusability highlights its substantial potential for industrial implementation.

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Chapter 6. Simple One-pot Fabrication of Durable Superhydrophobic Cotton Wool Using ODTMS Modified Silica-sol for Oil-water Separation

Abstract

A fluorine-free superhydrophobic cotton is successfully fabricated using a simple and cost-effective one-pot synthesis method, employing ODTMS as a modifying silane in a silica-sol. Unlike conventional techniques that utilise coupling agents or post-synthesis curing methods to enhance coating stability, this approach eliminates the need for extra chemicals thus saving time and reducing fabrication cost. The prepared cotton demonstrates remarkable superhydrophobicity, as evidenced by a WCA of 159°. Additionally, it exhibits exceptional durability and stability when exposed to harsh acidic and alkaline solutions, as well as during laundering test. Moreover, the cotton displays excellent oil-water separation efficiency (> 99.0%) and maintains consistent performance throughout 20 reuse cycles, highlighting its high reusability. Furthermore, the modified cotton is highly effective for separating oil-in-water emulsions, even for highly stable emulsions, achieving separation efficiencies above 90.0%. The fabrication process is simple and environmentally safe, offering an economical and viable solution for industries handling oily wastewater. Overall, this fluorine-free superhydrophobic cotton presents a promising and cost-effective option for various industrial applications.

6.1. Introduction

In recent years, there has been a concerning increase in global oil consumption and industrial activities, leading to a significant rise in the generation of oily wastewater.^{1,2} Discharging such wastewater into natural water bodies poses severe environmental risks, including contamination of aquatic ecosystems, formation of fatbergs in sewers, degradation of water quality, and threats to human health.²⁻⁴ Therefore, it is crucial for industries to develop efficient methods of separating

oil and water to mitigate environmental pollution caused by oil spills, industrial wastewater, and other oil-contaminated sources. However, traditional oil-water separation techniques like gravity settling, filtration, and flotation often suffer from limited efficiency, high energy consumption, and inadequate selectivity.^{5,6} As a result, there is a growing need to develop cost-effective and environmentally friendly materials for efficient oil-water separation.

Recently, superhydrophobic materials have emerged as promising candidates for oil-water separation due to their exceptional water-repellent properties and high affinities towards oils.⁷⁻⁹ These materials are characterised by their micro- and nanostructured topography, low surface energy, and the presence of trapped air pockets within their rough features.^{7,10,11} Consequently, superhydrophobic surfaces exhibit high WCA ($\geq 150^\circ$), resulting in no water droplets at the surface. These unique surface properties of superhydrophobic materials enable the selective adsorption and separation of oil from water, leading to highly efficient and sustainable oil-water separation processes. Various superhydrophobic materials, such as metal-based surfaces,¹² polymers,¹³ sponges,² and nanoparticles¹⁴ have been successfully explored for oil-water separation. However, they suffer from low oil sorption capacities, low separation efficiencies, and complex and time-consuming fabrication methods, hindering their practical application.

Among the prospective materials, natural fibres like cotton have gained considerable attention due to their widespread availability, renewability, and potential functionalisation. Cotton possesses inherent characteristics such as excellent adsorption capabilities due to its high porosity and surface roughness.¹⁵ However, cotton fibres possess hydrophilic properties due to a high density of hydroxyl groups, which make them readily absorb water and rendering them unsuitable for oil-water separation.¹¹ To overcome this limitation, often cotton is transformed into a superhydrophobic material by modifying its surface properties.^{6,16} This can be done through a variety of techniques, such as etching,¹⁷ spray coating,¹⁸ hydrothermal methods,¹⁹ sol-gel method²⁰ and others. These approaches aim to enhance the surface roughness and reduce the surface energy of the cotton.⁵ The resulting superhydrophobic cotton materials exhibit remarkable water-repellent

properties, allowing for the selective adsorption of oil. For example, Li et al.²¹ achieved 99.0% oil-water separation efficiency by immersion coating of polyvinylsilsesquioxanes and nano-aluminium oxide particles onto cotton fabric. Lv et al.²² fabricated superoleophilic cotton wool by attaching silica nanoparticles to the cotton surface through sol-gel method and subsequently functionalising it with octadecyltrichlorosilane. However, these methods often involve multiple steps, including curing, and require use of additional chemicals like coupling agents,^{18,23–25} leading to increased production costs and potential environmental concerns. The durability and reusability of superhydrophobic cotton wool are critical factors for its practical implementation.²⁶ The material's durability under harsh conditions, including high temperatures, pH variations, and mechanical stress, ensures its long-term effectiveness.²⁷ Furthermore, the ease of regeneration through simple techniques, such as heating or squeezing, allows for repeated use of the material, reducing waste generation and overall costs.

This chapter presents a low-cost and effective simple one-pot fabrication approach at room temperature to produce durable superhydrophobic cotton wool through co-hydrolysis and co-condensation of TEOS and ODTMS. The properties of the modified cotton, including surface morphology, surface chemical composition, wettability and durability were investigated. In addition, oil-water separation performance of the cotton was also tested. Due to the robust chemical bonding between the hydroxyl groups of cotton and the silanol groups of silica particles, coupled with the adhesive properties of the hydrophobic ODTMS, the modified cotton demonstrated remarkable chemical durability. Furthermore, owing to the long alkyl side chains of ODTMS and the surface roughness induced by the attached silica particles, the modified cotton displayed exceptional superhydrophobic characteristics (WCA = 159°). These unique properties made the modified cotton highly effective in separating oil from water in immiscible oil-water mixtures and efficiently demulsifying oil-in-water emulsions. This study presents a viable and sustainable solution for addressing industrial oily wastewaters, with particular relevance to the food industry

and food service establishments. It offers an effective means of mitigating the formation of fatbergs in sewer systems.

6.2. Materials and Methods

6.2.1. Cotton Pre-treatment

Acetone pretreated cotton, as outlined in Chapter 3, was heated in hexane at 60 °C for 1 h. Finally, it was dried at 60 °C until completely dry.

6.2.2. Synthesis of Superhydrophobic Cotton

To produce modified cotton sorbent, a mixture of ethanol (1.7 mol), DI water (0.6 mol), TEOS (30 mmol) and ODTMS (6.0 mmol) was prepared and mixed for 5 min at 500 rpm using a magnetic stirrer. ~1.0 g of pre-treated cotton was added to the mixture and left to soak for 5 min, with a polystyrene baffle used to separate cotton from the magnetic stirrer bar. Then, ammonia catalyst (80 mmol) was added dropwise to the mixture and the solution was left to react for 7 h at room temperature. The modified cotton was recovered and washed three times in ethanol to remove excess silica particles. The washed cotton was then dried in an oven (80 °C) until completely dry. The cotton was further treated with compressed air (~2.0 bar) until no powder was observed coming off from the sample. The dry weight gain (w) was calculated from equation 5.1 in chapter 5.

6.2.3. Characterisation

Sample characterisation were carried out, as outlined in chapter 3. For emulsion separation, 3.0 wt% oil-in-water emulsion was prepared by sonication of oil and water mixture for 1 h. The resulting emulsion was stable for 3 h at laboratory conditions. A piece of cotton sorbent was added to the emulsion and the separation process was facilitated by vigorous shaking. The separation efficiency was evaluated by measuring the total organic carbon (TOC) of the oil-water mixture before and after separation using the TOC analyser (Sievers innovox ES, Veolia Water

Technologies & Solutions, USA). The separation efficiency (E) was then determined using the following equation:

$$E(\%) = \left(\frac{TOC_0 - TOC_f}{TOC_0} \right) \cdot 100\% \quad (6.2)$$

Where TOC_0 is the TOC of the prepared emulsion and TOC_f is the TOC of the sample after separation.

6.3. Results and Discussions

6.3.1. Synthesis of Modified Cotton

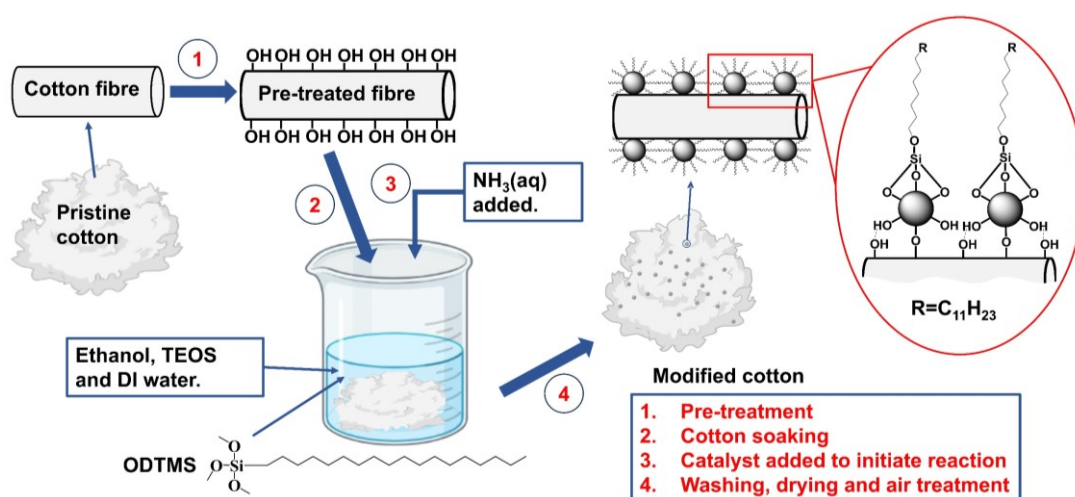


Figure 6.1 Schematic illustration of the synthesis process of superhydrophobic cotton.

The process involved in fabricating superhydrophobic cotton is illustrated in Figure 6.1. Initially, raw cotton was washed in acetone to eliminate solid impurities and any chemical impurities on the fibres that are soluble in acetone. Subsequently, the cotton was heated in hexane solvent to dissolve the organic wax layer present on the fibres. While other researchers often employ a highly concentrated NaOH for this purpose,²² it was observed (in chapter 5) that the pre-treatment with NaOH caused the fibres to clump together and reduced their absorbency. Additionally, it could potentially damage the cotton due to extreme pH. The post-treatment of the cotton also involves extensive washing to lower the pH to 7.

The removal of the wax layer on the cotton exposes the hydroxyl groups on the fibres, which then form bonds with silanol groups (-OH) present on the silica particles. These silica particles are

generated through the hydrolysis and condensation of TEOS and OTDMS. Despite the presence of a hydrophobic silane in the reaction mixture, not all the -OH groups of the silica particles react with the silane to create a hydrophobic surface. It is these unreacted silanol groups that enable the adherence of silica to cotton fibres through hydrogen bonding. Some studies have suggested the occurrence of covalent bonding between the -OH groups of cotton and those of silica particles.^{28,29} Although this claim lacks substantiation, it is included to consider its potential involvement in the attachment mechanism. An approximate 40.0% increase in dry weight before treating the samples with compressed air was observed, which then decreased to 25.0% after this treatment. This suggests that majority of the particles are physically trapped within the interstitial spaces of the cotton wool fibres.

6.3.2. Morphology and Wettability of Cotton

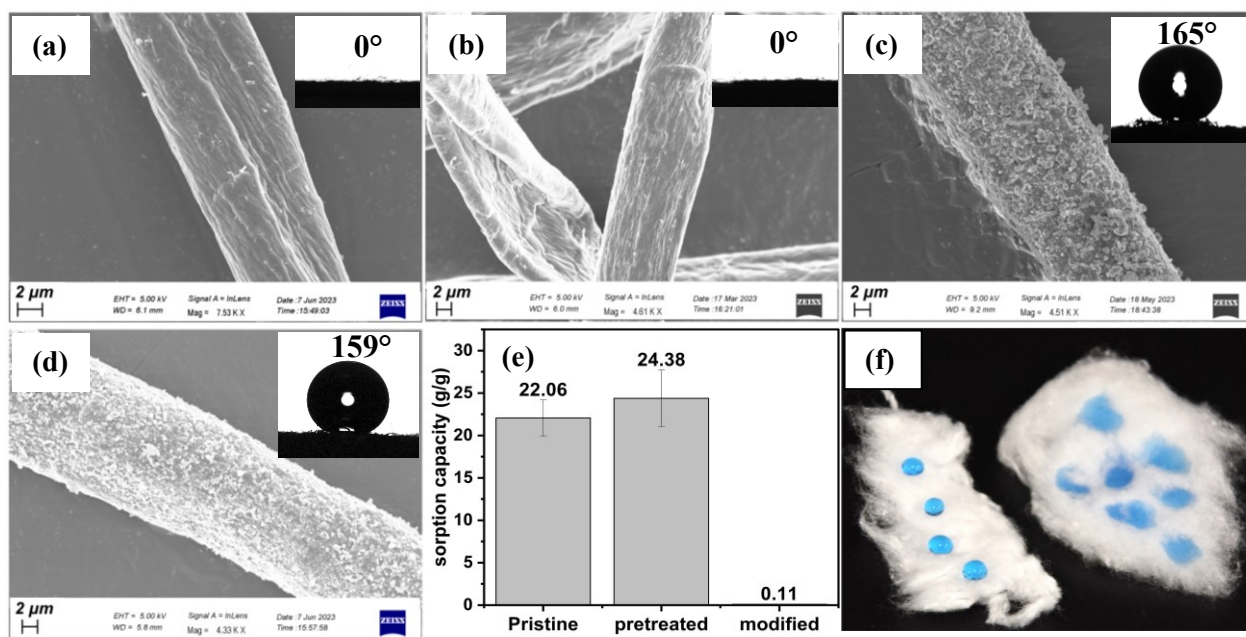


Figure 6.2 (a-d) SEM images of raw cotton, pre-treated cotton, superhydrophobic cotton before and after compressed air treatment, respectively. (e) and (f) water uptake of the cotton fibres and hydrophobic testing using blue dyed water.

The SEM imaging revealed that the pristine cotton fibres have subtle depressions, ridges, or lines on the surface of the cotton fibres, resembling the appearance of grooves or veins (Figure 6.2a) which is consistent with previous reports on cotton morphology.³⁰ However, contrasting findings have been reported in other studies, where smooth surfaces were observed for pristine

cotton.^{5,22} This disparity can be attributed to differences in the types of cotton utilised in the studies and the specific manufacturing processes employed for cotton treatment. No morphological differences between raw cotton and pre-treated cotton was observed.

However, upon modification, the cotton fibres exhibited a highly rough surface due to the micro-nano structures formed on the fibres by attached silica particles. Moreover, the modified cotton fibres displayed a uniform coating along the cotton fibre length, as depicted in Figure 6.2c. This well-structured and organised coating on the cotton surface can be credited to the inherent self-assembly nature of the silane.³¹ Nevertheless, after subjecting the cotton to compressed air to remove loosely adhered silica particles, some non-uniformity in the coating on the cotton fibres was noted (Figure 6.2d). It is evident that the one-pot fabrication method leads to a multi-layered coating on the fibre surface. The top layers are weakly attached to the first layer through hydrophobic interactions facilitated by the long alkyl chains of the grafted ODTMS silane. However, no substantial alteration in the morphology of the modified cotton following air treatment was noticed. The robustness of this silica particles' attachment as demonstrated by the SEM images can be attributed to the oily nature of hydrophobic silanes, which is a result of their elongated alkyl chains. These properties confer adhesive capabilities to the silane, allowing for effective attachment of silica particles.

To determine the degree of surface modification, the hydrophobicity of the surface was assessed using WCA measurements. The purpose of hydrophobic modification is to enhance the preferential selectivity of cotton for oil rather than water. Therefore, the water sorption behaviour of cotton fibres was also investigated. As seen from the WCA inserts in Figure 6.2(a-b) pristine and pre-treated cotton have WCA of zero, indicating their hydrophilic nature. In contrast, the modified cotton displayed remarkable superhydrophobicity (WCA~159°) attributed to the elongated alkyl chains of ODTMS, which effectively reduce the surface energy. Additionally, the increased surface roughness of the modified fibres due to silica particles further improves the hydrophobicity of the surface.³² This is evident on the modified cotton before the removal of excess

silica particles by air treatment, which displayed WCA of 165° . Lin et al.²⁰ showed that it is possible to achieve superhydrophobicity on cotton using hydroxyl-terminated polydimethylsiloxane without any curing or coupling agents. The superhydrophobicity of the modified cotton is also evident in Figure 6.2f, where blue-dyed water droplets remain spherical on the modified cotton but absorb on the pristine cotton. During the water sorption investigation (Figure 6.2e), both pristine and pre-treated cotton soaked in water and exhibited high water sorption capacities (~ 22.0 and 24.0 g/g, respectively). Conversely, the superhydrophobic cotton floated and displayed minimal water uptake (~ 0.1 g/g) despite being submerged, owing to its highly water-repellent surface. These results confirmed the successful hydrophobic modification of cotton fibres.

6.3.3. Chemical Properties of Cotton

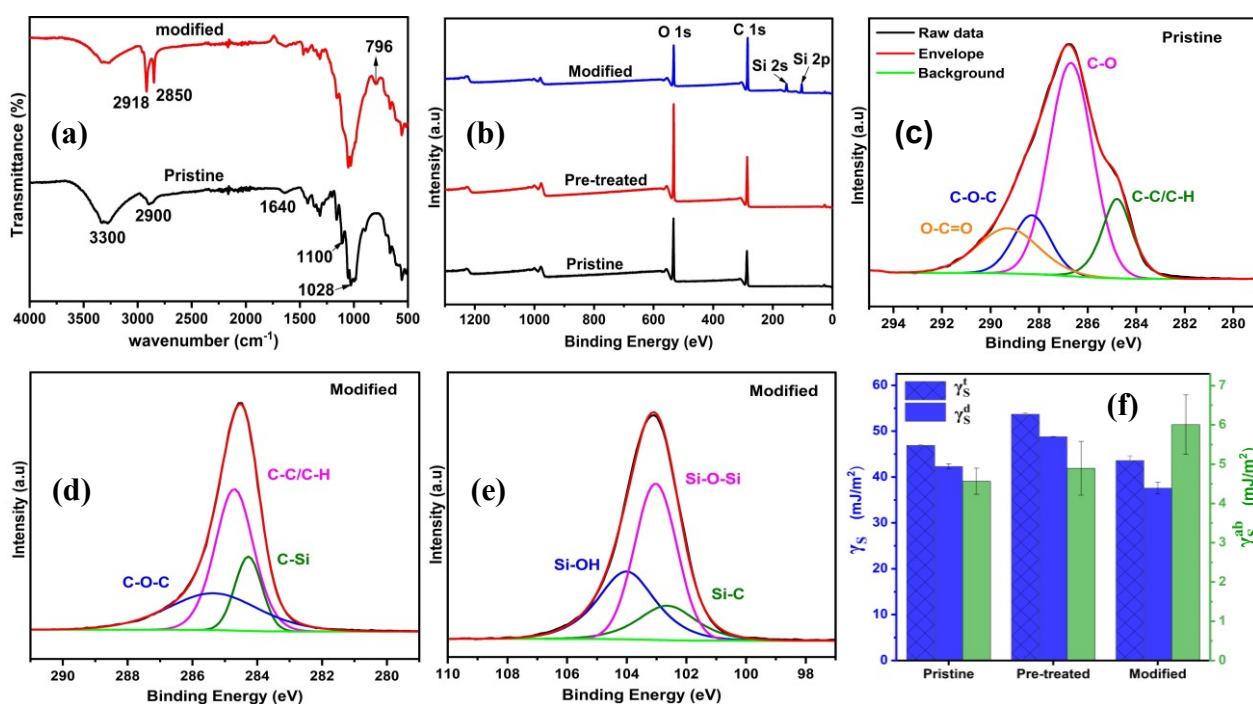


Figure 6.3 (a-b) FTIR spectra and XPS survey of cotton samples, respectively. High resolution spectra of C 1s core level of (c) pristine cotton, (d) modified cotton. (e) High resolution spectra of Si 2p of modified cotton. (f) Surface energy of cotton.

The bulk chemical structure of cotton samples was analysed using FTIR as depicted in Figure 6.3a. The spectra revealed significant peaks, including the broad peak at 3300 cm^{-1} attributed to OH bond stretching of hydroxyl groups of cellulose and any adsorbed water.²⁴ Another peak at 1640 cm^{-1} indicated the presence of adsorbed water.³³ The peaks at 1028 , 1100 and 2900 cm^{-1} corresponded to C-O stretch, asymmetric bridge C-O-C and C-H stretching, respectively.^{24,33} The

modified cotton showed new peaks as well as disappearance of the 1100 cm⁻¹ peak. The new peaks at 796 and 2850 cm⁻¹ indicated Si-O-Si symmetric stretching due to silica particles,³⁴ and CH₂ asymmetric stretch of long alkyl chains grafted on the cotton,³³ respectively.

XPS was employed to verify the surface chemistry of the fibres and surface elemental composition. As shown in Figure 6.3b, both pristine and pre-treated cotton surfaces were primarily composed of oxygen and carbon, with oxygen proportions of 37.6% and 38.1%, respectively. In contrast, the modified cotton surface exhibited additional silicon peaks (Si 2s and 2p), confirming the presence of modified silica particles. Moreover, the modified cotton surface comprised 12.9% silicon, 62.6% carbon, and 24.5% oxygen elements. The C 1s core level spectra of the pristine and modified cotton samples are shown in Figure 6.3c,d. The C 1s for pristine cotton showed characteristic peaks to C–C/C–H (284.8 eV), C–O (286.7 eV), O–C–O (288.5 eV) and O–C=O (290.1 eV). These peaks represented alkyl chains, hydroxyl groups of cellulose and β-1,4-glycosidic bonds linking glucose chains of cellulose. The O–C=O peak is due to the lipid component of the wax layer.^{35,36} The same constituents were observed for pre-treated cotton C 1s spectrum (Figure A.4 in the appendix) but with a lower intensity of the O–C=O peak. As for modified cotton, the C 1s spectrum consisted of C–Si (284.3 eV) and C–C (284.7 eV), O–C–O (285.4 eV), from cellulose and the ODTMS modified silica particles.^{37,38} Furthermore, the intensity of the C–C/C–H increased because of the grafted alkyl chains of the silane.²⁴ The Si 2P spectrum (Figure 6.3e) of modified cotton consisted of Si–C (102.6 eV) peak from ODTMS silane, Si–O–Si (103.0 eV) and Si–OH (104.0 eV) peaks from silica particles.

Surface energy analysis of the cotton samples was conducted to investigate the effects of modification on cotton fibres (Figure 6.3f). The γ_S^d and γ_S^{ab} components of surface energy were determined and the total surface energy (γ_S^t) calculated as the sum of γ_S^d and γ_S^{ab} . The γ_S^d originates from the Van der Waals interactions between solvent probes and the cotton surface, whereas the γ_S^{ab} is due to polar probe-surface interactions. The analysis confirmed the reduction in total surface energy of the modified sample. However, the γ_S^{ab} was high for modified cotton (6.0 mJ/m²)

compared to pristine (4.6 mJ/m²) and pre-treated (4.9 mJ/m²) cotton samples. This was due to the unmodified parts of the silica particles, which increased the polarity of cotton because of the silanol groups. Given that the probes used for surface energy analysis are in the gas phase, they can reach these silanol groups despite being shielded by the long alkyl chains of the ODTMS. In the context of WCA measurements, this shielding effect effectively prevents water droplets from accessing the silanol groups, hence higher WCA measured. Despite higher γ_S^{ab} , the γ_S^d of the modified cotton was lower by $\sim 22.0\%$ compared to the pre-treated cotton, which displayed a high value (48.8 mJ/m²) among all three samples due to removal of wax.³⁹ Consequently, the total surface energy of the modified cotton samples decreased by about 19.0%. The predominance of Van der Waals forces over polar interactions in the adsorption of probe molecules to the surface was evident, as indicated by higher γ_S^d than γ_S^{ab} for all samples. Similar surface energy values have been reported for cotton fibres using IGC technique.^{40,41}

6.3.4. Thermal Properties of Cotton

Thermal properties of the cotton fibres were investigated using TGA analysis under air and nitrogen atmospheres. Figure 6.4a,b illustrates distinct thermograms for the fibres under these two atmospheres. Although not shown here, samples displayed a region of weight loss below 100 °C because of loss of moisture and volatiles in the samples. For temperatures above 100 °C, pristine and pre-treated cotton samples burned under nitrogen displayed a single region of weight loss between 280 and 385 °C. This rapid and significant weight loss is due to pyrolysis of the cellulose structure of cotton into a levoglucosan residue.²⁰ However, modified cotton exhibited an additional weight loss region from 400-700 °C due to the removal of -OH groups from silica particles (Figure 6.4c).

Under air atmosphere, samples showed two weight loss regions above 100 °C, except for modified cotton, which displayed an extra region between 200 and 300 °C. The weight loss from 260-350 °C resulted from cellulose network dehydration and decarboxylation,^{42,43} while the subsequent region (350-500 °C) was due to oxidative degradation of the formed char residue.⁴⁴ The

sudden weight loss between 200 and 260 °C is due to decomposition of the alkyl chains of ODTMS silane. Modified cotton in both TGA atmospheres exhibited higher residual weight due to the presence of thermally stable silica particles. Under nitrogen gas, modified cotton displayed a residual weight of 19.0%, compared to 8.0% and 8.9% for pristine and pre-treated cotton samples, respectively. Similarly, in an air atmosphere, modified cotton showed 19.1% residual weight, in contrast to 0.4% and 1.8% for pristine and pre-treated samples, respectively.

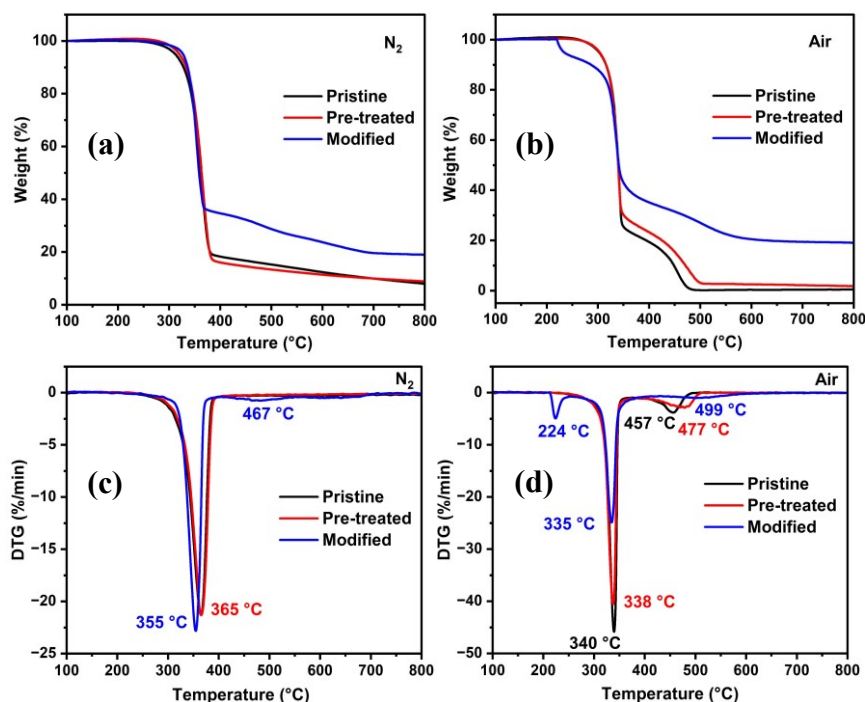


Figure 6.4 TGA and DTG curves of pristine, pre-treated, and modified cotton under (a, c) nitrogen and (b, d) air atmosphere.

The DTG curves in Figure 6.4c,d represent the temperatures at the maximum rates of weight loss in different temperature regions. The region of the most substantial weight loss occurred at slightly higher temperatures under the nitrogen atmosphere compared to samples burned in air. Additionally, the greatest rate of weight loss was higher for samples burned in air compared to nitrogen gas. However, modified cotton showed a lower weight loss rate when burned in air compared to pristine and pre-treated samples. This is due to the superhydrophobic coating by silica particles which reduces heat transfer to the cotton fibres, thereby decreasing their degradation rate.²⁰

6.3.5. Durability Test of Modified Cotton

The high durability of modified cotton is a critical and desirable property for industrial applications. Under harsh process conditions, superhydrophobic layer on the cotton may suffer corrosive chemical attack or mechanical degradation, impacting its performance. Therefore, it is paramount to investigate the durability of the modified cotton. Chemical and pH durability tests were conducted by immersing the cotton in various solvents and solutions with pH ranging from 2 to 13, followed by measuring the WCA. As shown in Figure 6.5a, the WCA decreased from 159° to ~155° under extreme pH conditions (pH 2 and 13), indicating high pH durability of the modified cotton. Additionally, a minor decrease of approximately 4° and 3° in WCA was observed for cotton samples immersed in NaCl (3 M) and hot water (60 °C), respectively. However, no significant change in WCA was observed for other solvents, demonstrating the modified cotton's high chemical durability.

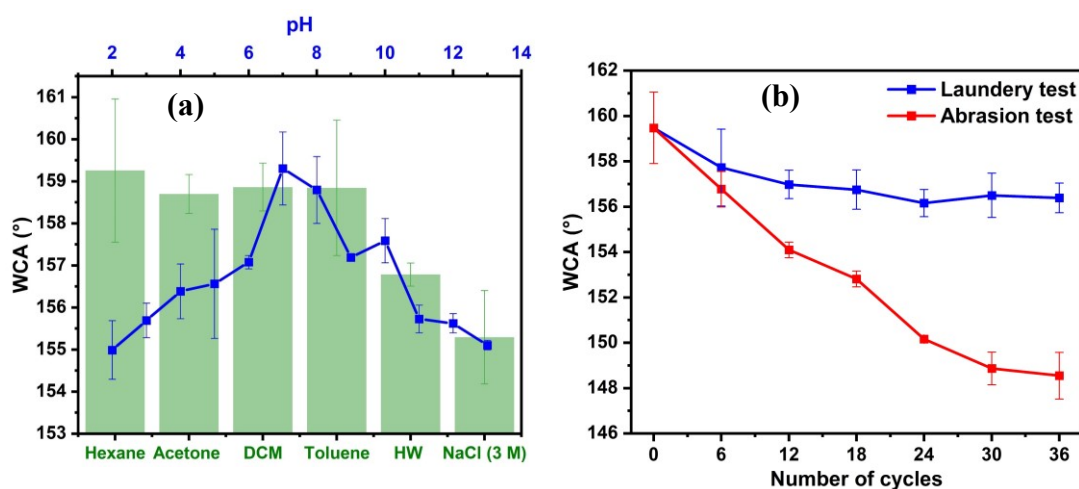


Figure 6.5 WCA of the modified cotton after (a) pH and chemical durability testing, (b) Laundering and abrasion testing.

The laundry test was carried out to test the durability of modified cotton wool in a detergent water solution. As illustrated in Figure 6.5b, WCA remained almost unchanged, with only a slight reduction of approximately 2°, indicating the modified cotton's superior superhydrophobicity. This minor change could be attributed to the removal of bilayer particles on the coating that were attracted to each other through hydrophobic interactions. The mechanical stability of the modified

cotton was assessed using an abrasion test (Figure 6.5b). After 36 test cycles, the WCA significantly dropped from 159° to around 148°, and superhydrophobicity was maintained only for 24 cycles. This decline can be attributed to the removal of attached particles on the coating due to the heating effect caused by friction during the rotation of the load. The frictional heat generated, along with the rough surface of the sandpaper, can disrupt the bonding between cotton and silica particles.

In conclusion, the fabricated cotton demonstrated excellent durability under various harsh conditions while maintaining its superhydrophobicity. The results suggest that silica particles are strongly bonded to the cotton, possibly even through covalent bonding, as previously reported.²⁹ As a result, this modified cotton holds significant potential for industrial applications under various severe environmental conditions.

6.3.6. Oil-water Separation

Superhydrophobic materials have shown remarkable efficacy in removing oils from oily wastewater.^{28,32} In this study, the oleophilicity and oil-water separation properties of one-pot modified cotton were investigated using different cooking oils. The goal was to assess whether the cotton sorbent could be utilised in food service establishments and the food industry to mitigate oily wastewater and reduce FOG deposits in sewers. Cooking oils, unlike most organic oils, contain amphipathic molecules such as phospholipids and free fatty acids. As a result, the use of the gravimetric method may overestimate the separation efficiency due to adsorbed water droplets at the oil-water interface; hence the use of UV-Vis spectrometer.

The oil-water separation process is shown by images in Figure 6.6a, where olive oil (dyed with Oil Red O) was used. As depicted, the modified cotton demonstrated excellent oleophilicity by selectively absorbing all the oil from the water surface. Furthermore, maximum oil sorption capacities of the fabricated cotton were determined for different oils (Figure 6.6c). The modified cotton displayed high oil sorption capacity for olive oil (43.6 g/g), followed by vegetable, rapeseed and sesame oils which displayed similar sorption capacities (~40 g/g). Sunflower oil showed the

lowest sorption capacity among all tested oils at 37.5 g/g. This observed trend can be attributed to the viscosity of the cooking oils, which influences the flow of oil into the cotton. Olive oil is more viscous than the other oils used,⁴⁵ followed by vegetable, rapeseed, sesame oils and sunflower which have similar viscosities.^{45,46} Higher viscosity leads to slower flow of the oil out of the cotton once absorbed, resulting in better retention within the cotton. Conversely, less viscous oils absorb quickly into the cotton sorbent due to their easy flow. However, during the draining of excess oil before weight measurements, a significant portion of the oil is also lost, particularly with oils of lower viscosity. The oil sorption capacities observed in this study for olive and sesame oils surpass those previously reported (36.1 and 37.1 g/g, respectively).³⁰

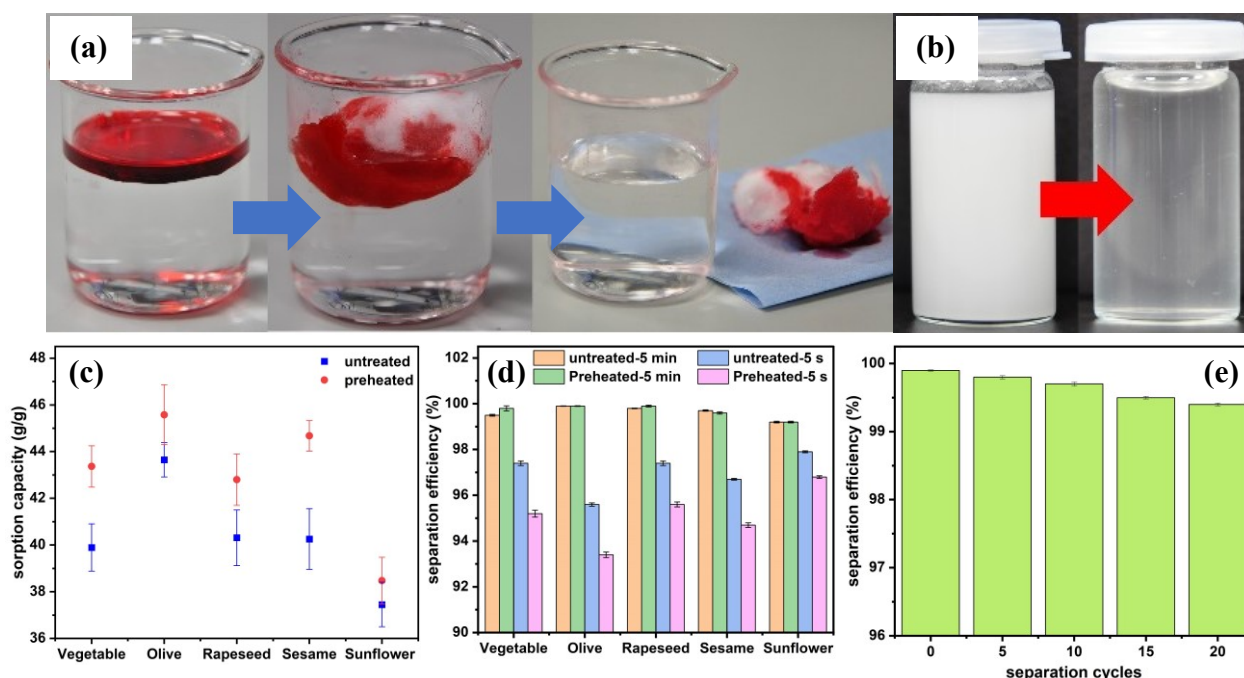


Figure 6.6 (a) Photographs of (a) olive oil separation from water surface and (b) olive oil-in-water emulsion separation. (b) maximum oil sorption of modified cotton in pure oils. (c) oil-water separation efficiencies of different cooking oils. (e) reusability of cotton sorbent for olive oil-water mixture separation over 20 test cycles.

Effects of heating were also investigated as certain oils undergo heat treatment in the food industry, such as deep frying, which is common in most food service establishments. The cooking oils were heated to 160 °C and then cooled to room temperature before determining their oil sorption capacities by the modified cotton. The results revealed that heating the oils increased their sorption capacity to the cotton. This is attributed to hydrolysis, oxidation, and polymerisation of the oil components, such as unsaturated fatty acids.^{47,48} These reactions result in increased viscosity

of the cooking oils,^{47–50} consequently enhancing their sorption capacities to the modified cotton.

Additionally, the oil-water separation efficiency of the modified cotton was examined for all the cooking oils (Figure 6.6d). Due to their low density, the oils floated on the water surface, making this type of separation easy and rapid. The modified cotton showed separation efficiencies higher than 99.0% for all oils within a 5 min contact time, highlighting its remarkable sorption ability. Notably, there was no significant difference in the sorption efficiency of the sorbent between the various oils used. This can be attributed to the 5 min contact time used, which proved sufficient to overcome mass transfer limitations in the separation process. The residual oils detected may be due to the oil adhering to the glass container walls used during the separation process. It may also be from the oil that drip off from the cotton due to hydrophilic attachment at the oil-water interface between certain oil constituents and water molecules. At a shorter contact time of 5 s, separation efficiencies decreased for all oil samples, with the lowest recorded for preheated olive oil at 93.4%. This is because at short contact time mass transport of the oil into the modified cotton becomes relevant and impact separation performance. Nevertheless, the decrease was not drastic, suggesting that the modified cotton can still rapidly absorb oil even under short contact times. Furthermore, all preheated oil samples displayed lower sorption capacities compared to untreated oil samples for the same oil type. The increased viscosity of preheated oils indicates increased resistance to flow, leading to reduced mass transfer into the cotton and limiting their absorbability. The usability of the modified cotton was tested for 20 separation cycles using untreated olive oil and a 5 min contact time. After each cycle, the cotton was regenerated by squeezing and washing in a small amount of hexane to remove residual oil. Throughout all 20 separation cycles, the cotton maintained high separation efficiency (> 99.0%) as depicted in Figure 6.6e. These results show that the ODTMS modified cotton exhibits rapid and efficient oil removal from water, along with excellent recyclability.

Furthermore, the superhydrophobic cotton was assessed for its ability to remove oil from oil-in-water emulsions without surfactants. Superhydrophobic materials have demonstrated incredible

success in demulsifying oil-in-water emulsions, including those stabilised by surfactants.^{8,51,52} In contrast to research focused on water-in-oil emulsions, which frequently utilises filtration separation, the aforementioned investigations involve immersing the material into the emulsion, either with or without agitation. This approach is adopted due to the fact that the continuous phase of these emulsions is water, and superhydrophobic materials completely repel water. As a result, filtration is not conducive to achieving effective separation. As shown in Figure 6.6b, the cotton was effective in removing oil from the emulsion, resulting in the solution changing from milky white to a clear, slightly turbid solution within 1 min. However, the separation efficiency (~90.0%) was relatively low due to the high stability of the emulsion. In contrast, for low stability emulsions prepared by shear mixing using a magnetic stirrer, the modified cotton displayed a significantly higher separation efficiency of 98.2% (Figure A.5 in the appendix). Demulsification is driven by the interplay of intermolecular attractive forces between the dispersed oil phase and the superhydrophobic cotton surface, as well as repulsive forces between the continuous water phase and the same cotton surface.^{53–55} This interplay results in the destabilisation of the emulsion, causing the flocculation and coalescence of oil droplets and ultimately leading to demulsification.⁵⁴

Therefore, the modified cotton can be effectively applied upstream in emulsion separation processes to reduce oil concentration in the emulsions and alleviate the load on downstream process units.

6.4. Conclusions

In summary, a highly durable and superhydrophobic cotton sorbent with exceptional oil-water separation capabilities was successfully developed. The modified cotton was fabricated using a simple and cost-effective one-pot synthesis, employing TEOS as a silica precursor and ODTMS as a modifying silane. The resulting cotton exhibited a high WCA of 159° and minimal water sorption, confirming its superhydrophobic nature. The prepared cotton demonstrated remarkable resistance to various organic solvents, as well as acidic and alkaline solutions, when immersed. Additionally, it displayed outstanding durability during laundering tests. The superhydrophobic

cotton's high oleophilicity enabled successful separation of oil from different types of cooking oil-water mixtures, achieving impressive separation efficiencies (> 99.0%). The fabricated cotton also proved to be highly reusable, maintaining similar separation efficiency even after 20 separation cycles. Furthermore, the cotton sorbent effectively tackled oil-in-water emulsions, even those that were highly stable. Its combination of high-water repellence, excellent durability, exceptional oil-water separation performance, and reusability showcases its strong potential for industrial implementation.

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Chapter 7. Synthesis of Superhydrophilic Cellulose Materials to Remove Oil from Oil-in-water Emulsions Before Disposal of Wastewaters to Sewers

Abstract

Oil-emulsified wastewaters pose a widespread challenge across various industries due to their remarkable stability, making their separation a formidable task. Drawing inspiration from bio-structures such as fish scales, innovative superwetting materials have been successfully developed and implemented for the separation of oil-in-water emulsions. In dealing with FOG deposits in sewers, the prevailing approach involves the use of immiscible oil-water separators exclusively. Hence, it is imperative to extend the application of oil-in-water emulsion separation technology to address FOGs at their origin sources. Herein, superhydrophilic cellulose materials, including cotton, tissue paper and others, were employed for the separation of oil-in-water emulsions derived from cooking oils and recovered oils from grilling salmon and chicken. A straightforward dip coating method was utilised to synthesise superwetting cellulosic surfaces using Polyethylenimine (PEI) and polyvinylpyrrolidone (PVP) polymers. Driven by both gravity and applied pressure of 0.1 bar, the coated materials successfully separated oil-in-water emulsions, consistently achieving separation efficiencies exceeding 99.0%. Notably, modified cotton wool exhibited superior performance across various oil emulsions, whether surfactant-stabilised or free, with separation efficiencies consistently surpassing 99%. Furthermore, even after 20 cycles of reuse, the treated cotton maintained a separation efficiency of over 97.0%. This underscores the potential of superhydrophilic materials as a viable solution to address the fatberg issue by removing FOGs that find their way into sewers through oil-in-water emulsion wastewaters. The method used in this study also offers a simple and effective alternative for producing superwetting filters designed for emulsion separation.

7.1. Introduction

The preceding chapters (chapter 4, 5 and 6) demonstrated the efficacy of superhydrophobic materials in efficiently separating immiscible oil and water, even in the presence of congealed fats. Despite this remarkable performance, the superhydrophobic cotton prepared was found to be ineffective for highly stable oil-in-water emulsions.

Oil-in-water emulsions, ubiquitous in industrial processes and environmental contaminants, pose a formidable challenge due to their complex and stable nature.^{1,2} This poses a significant challenge, particularly in the context of fatbergs, as emulsions find their way into sewers. Over time, the bacteria within the sewers can break down these emulsions.³ The destabilised emulsions then undergo separation into their constituent phases, namely oil and water. The accumulation of this oil can subsequently contribute to the formation of fatbergs. Conventional methods commonly used for oil-in-water emulsion separation include centrifugal force, electrostatic precipitation, cyclones, physical or chemical demulsification, heat treatment, etc⁴ However, these techniques often fall short in addressing the intricacies of such emulsions due to their low separation efficiencies, complex operational procedures, and high associated costs.^{5,6} This necessitates innovative approaches that can selectively and effectively separate oil and water from stable emulsions. Superhydrophilic materials, with their exceptional affinity for water and ability to promote rapid wetting, present a promising avenue for achieving precision control in oil-in-water emulsion separation processes.^{7,8}

At the core of the fascination surrounding superhydrophilic materials lies in their ability to attract and disperse water on their surfaces rapidly. This unique property, stemming from robust interactions between the material and water molecules, provides an underwater superoleophobicity feature for facilitating the separation of oil-in-water emulsions.⁹ Understanding the molecular dynamics of interfacial forces and surface interactions becomes crucial in designing materials that can promote rapid wetting and, subsequently, effective extraction of FOG constituents from the water matrix. Recent advancements in material science have witnessed the synthesis of

superhydrophilic materials with enhanced selectivity for oil-in-water emulsion separation. From innovative nanostructures to bio-inspired designs, the spectrum of superhydrophilic materials has expanded, offering a diverse toolkit for addressing the challenges posed by oil-in-water emulsions.¹⁰ Du et al.¹¹ fabricated a superhydrophilic composite membrane using chitosan and titanium dioxide, which showed superior oil-in-water emulsions separation with 97% separation efficiency. These bio-inspired materials offer more cost-effective and environmentally friendly solutions to oil-in-water emulsion challenges.¹² Superhydrophilic materials, with their potential for high efficiency and selectivity, offer a pathway to optimise processes, reduce energy consumption, and enhance the overall economic viability of oil-in-water separation techniques. However, these materials have not been explored as a solution towards the prevalent fatberg problem in urban areas.

Hence, this study delves into the exploration of superhydrophilic/superwetting cellulosic materials for the separation of oil-in-water emulsions. The objective is to assess the viability of the manufactured materials as a potential solution for FOGs that infiltrate sewer systems through emulsified oily wastewater. The one-pot coating method was employed to craft superwetting surfaces on cotton wool, tissue paper, used tea leaves, and tea bags, utilising a solution comprising PEI and PVP. The hydrophilic polymer coating was affixed to the substrates through hydrogen bonding, and the adhesive nature of PEI contributed to enhanced attachment. Remarkably, the modified substrates, except for used tea leaves, demonstrated exceptional performance in separating oil-in-water emulsions (> 99.0%). The noteworthy efficiency of these materials, combined with the simplicity of the fabrication process and the cost-effectiveness of readily available substrates, suggests their potential application in addressing FOG-laden emulsions.

7.2. Materials and Methods

7.2.1. Materials

Tissue paper, Branched PEI ($M_w \sim 800$) and PVP ($M_w \sim 40\,000$) were purchased from Sigma Aldrich (Gillingham, UK). Used green tea leaves and used tea bags were sourced from a domestic kitchen.

7.2.2. Synthesis of Superhydrophilic Materials

Firstly, 3.0 g of cotton was washed twice in acetone and dried in a vacuum oven (60 °C, 200 mbar) for 1 h. The coating solution was formulated by mixing 1.0 wt% of PEI with 150 mL of DI-water, followed by addition of PVP (1.5 wt%). The solution was vigorously mixed until the complete dissolution of PVP. The acetone-washed cotton was then immersed in the prepared solution for 2 h. Subsequently, the modified cotton was dried in an oven at 80 °C, followed by a curing process at 120 °C for 5 min. The cured cotton underwent a DI-water wash to eliminate any residual PVP coating.

In addition to cotton, various substrate materials such as tissue paper, used tea leaves, and tea bags were also coated using the aforementioned procedure.

7.2.3. Material Characterisation

Only materials exhibiting high performance were characterised following their initial assessment of emulsion separation efficiency. Only SEM, TGA and XPS characterisation were carried out, as outlined in chapter 3.

7.2.4. Preparation of Emulsions

Surfactant stabilised oil-in-water emulsions of 5.0% v/v oil concentration were prepared by adding 5 mL oil (sunflower, olive oil, rapeseed and oven grill recovered oils from chicken and salmon) to a mixture of tap water (95 mL) and SDS surfactant (100 mg). This was followed by vigorous mixing with a magnetic stirrer to produce a highly stable emulsion with over 24 h stability time.

Non-surfactant stabilised emulsions of the same concentration (5.0% v/v) were prepared following a similar procedure above in the absence of a surfactant. The mixtures were sonicated to disperse oil droplets in water and create an emulsion. The resulting emulsions were stable at room temperature for 3 h.

7.2.5. Emulsion Separation Experiment

A piece of modified sample (~ 1.0 g) was added to a 60 mL syringe tube, with a stainless-steel mesh used as a support. The cotton was wetted with water and compressed tightly prior to separation analysis. Following this preparation, an emulsion was then poured into the syringe tube and separated employing a gravity-driven process. The flux (F) was subsequently determined by calculating the filtration time of a 30 mL emulsion feed using the following equation:

$$F = \frac{V}{At} \quad (7.1)$$

Where V is the filtrate volume collected, A and t are the correctional area and filtration time. Similar separation process was repeated with external applied pressure of 0.1 bar. Oil concentration in the filtrate was determined using the UV-Vis spectrometer. The separation efficiency was then calculated from:

$$E = \frac{C_{feed} - C_{filtrate}}{C_{feed}} \times 100\% \quad (7.2)$$

where C_{feed} and $C_{filtrate}$ are the feed and filtrate oil concentrations.

7.3. Results and Discussions

7.3.1. Preparation of Superwetting and Superoleophobic Materials

The preparation process of superhydrophilic cotton wool is illustrated in Figure 7.1 and the chemical structure of the polymers is depicted in Figure 7.2. Pre-treatment of cotton allows removal of dust and any impurities which may hinder the coating process. PEI enhances the attachment of the PVP polymer to the cotton surface through hydrogen bonding between its $-NH_2$ groups and cotton's hydroxyl groups,¹³ as shown by the chemical structure in Figure 7.2. Moreover, the inherently adhesive nature of PEI contributes to an enhanced attachment during the coating process. The PVP polymer coating on the cotton and other substrates enhances their surface energy resulting in the manifestation of their superhydrophilic or underwater superoleophobic properties.^{9,14}

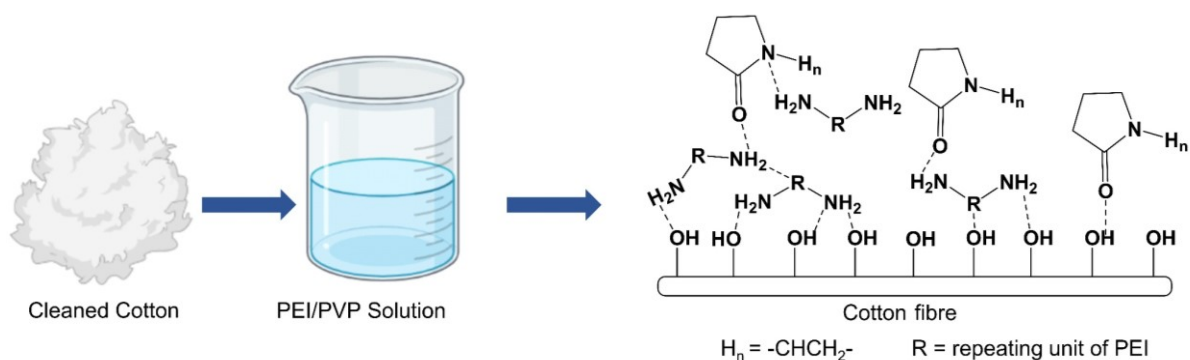


Figure 7.1 Synthesis of superhydrophilic through dip coating method.

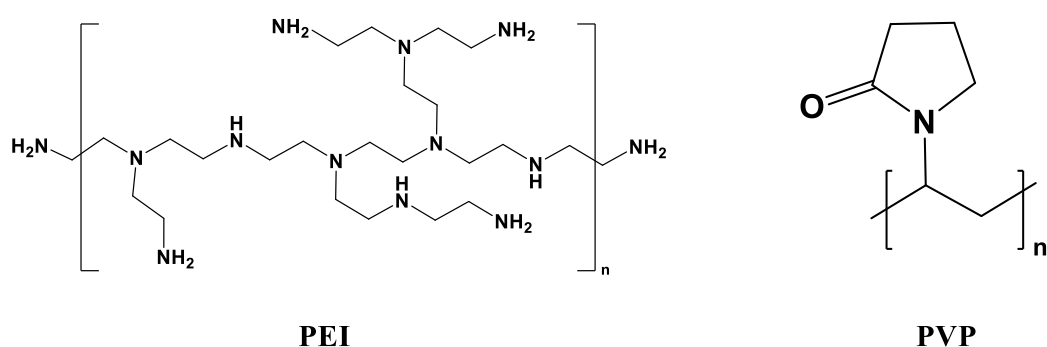


Figure 7.2 Chemical structure of the PEI and PVP polymers.

7.3.2. Morphology of Cotton and Tissue paper

Following the preliminary emulsion separation performance test, coated cotton wool and tissue paper samples were chosen for characterisation analysis. The morphology of these samples was observed using SEM imaging. As shown in Figure 7.3a,b, unmodified samples displayed smooth surfaces with ridges and grooves. Modified samples, as shown in Figure 7.3c-f, exhibited a polymer coating on cellulose fibres, leading to increased surface roughness. However, it can also be seen that the coating on the fibres appears inconsistent, with some areas seeming to be uncoated. In summary, the SEM images confirm the successful coating of the cotton wool and the tissue paper substrates. During compression for emulsion separation, the coating reduces interstitial spaces between fibres and particles. Additionally, the adhesive nature of PEI promotes the attachment of fibres/particles together, forming an efficient separation filter.

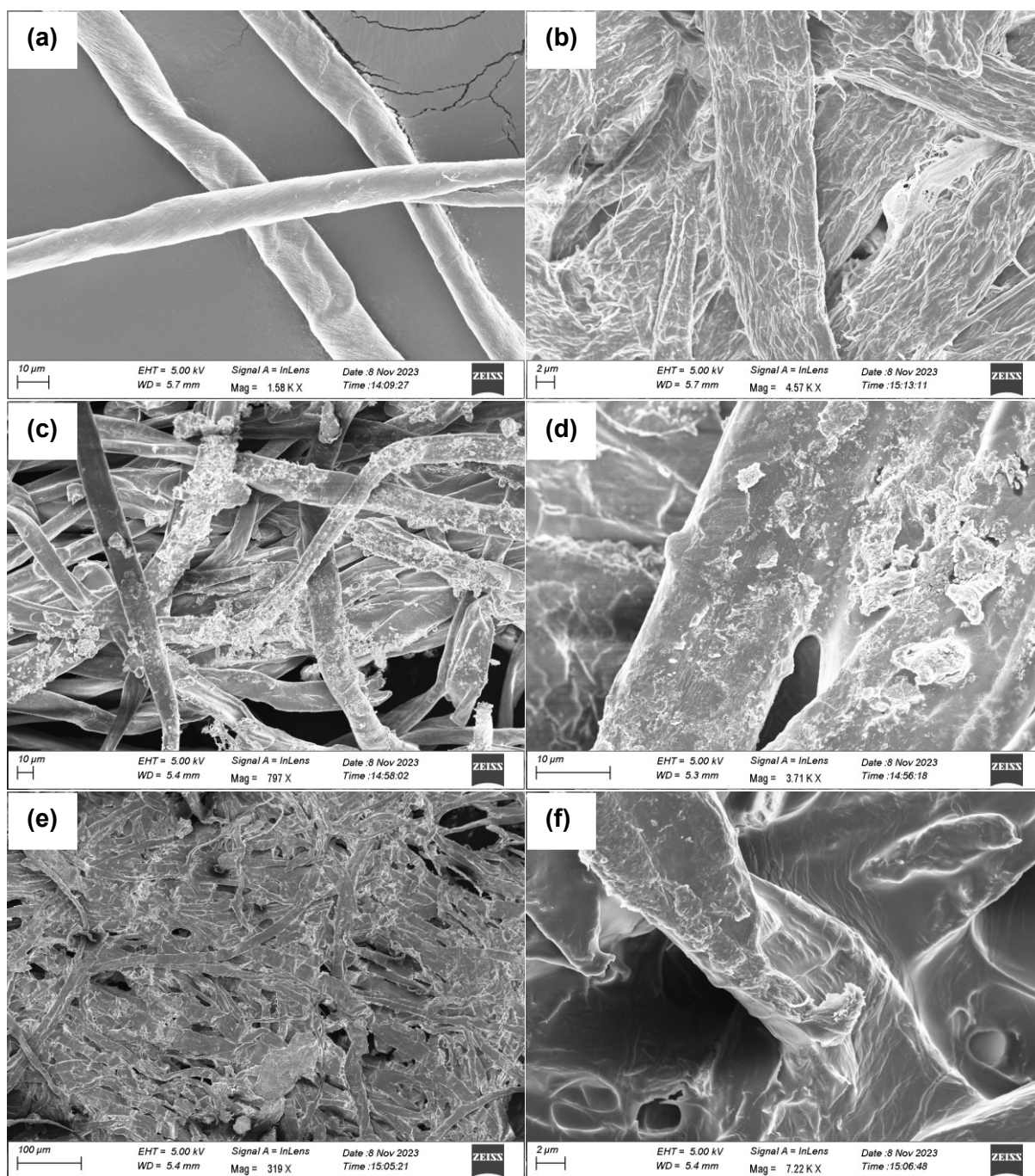


Figure 7.3 SEM imaging of cotton and tissue paper. (a-b) Pristine cotton and tissue paper, (c-d) coated cotton at low and high magnification, respectively, (d-e) coated tissue paper at low and high magnification, respectively.

7.3.3. Surface Chemistry Analysis and Thermal Properties

Surface chemical properties and composition of the modified cotton wool and tissue paper were assessed using XPS. As shown in the XPS survey spectra (Figure 7.4a), the unmodified samples primarily featured carbon and oxygen atoms inherent to the cellulose structure of these materials.

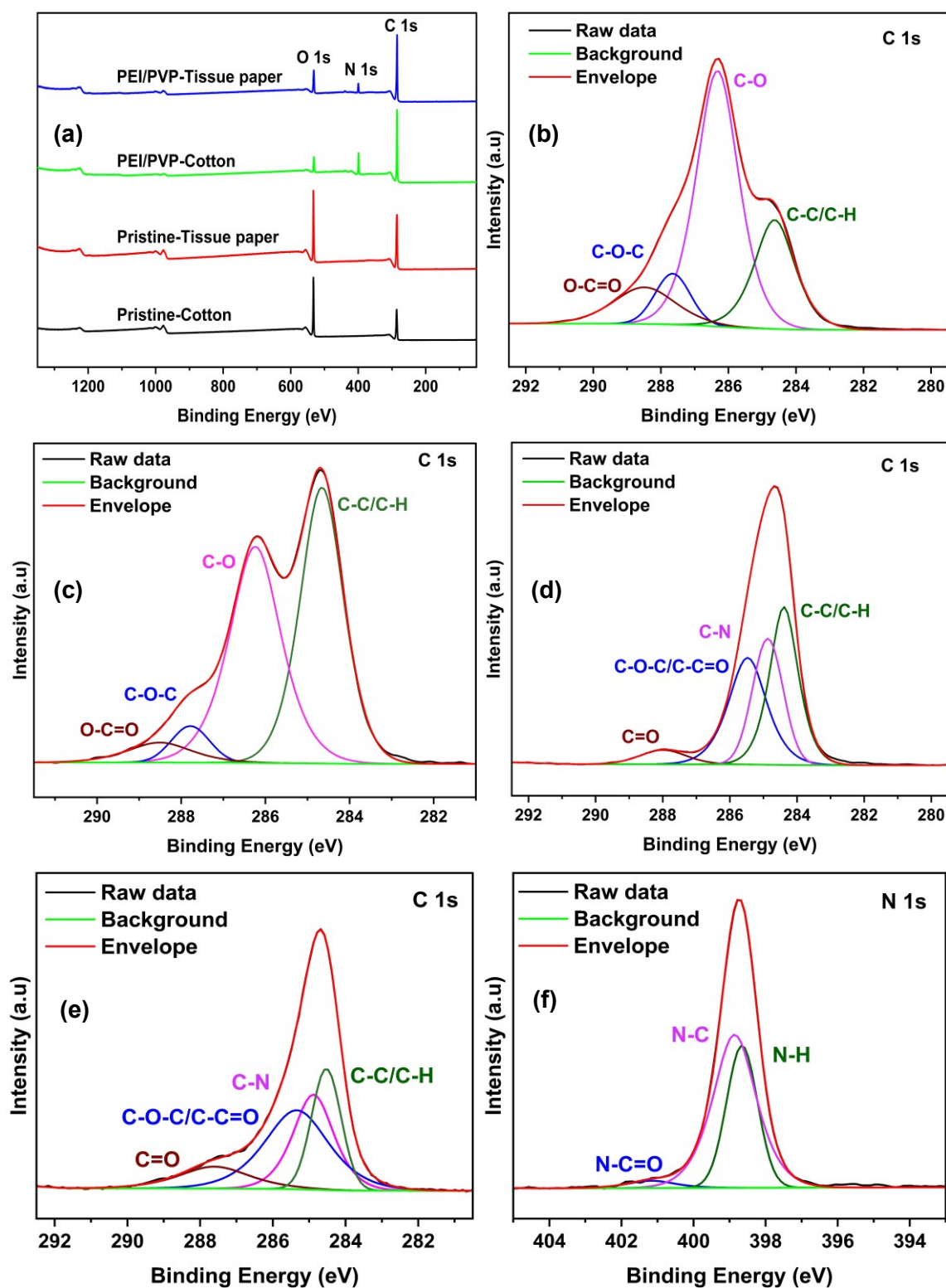


Figure 7.4 (a) XPS survey of uncoated and coated tissue paper and cotton wool. (b-e) High resolution analysis of the C 1s core level of (b,c) pristine cotton and tissue paper, respectively, (d,e) coated cotton and tissue paper, respectively. (f) Deconvoluted N 1s core level of coated cotton.

Specifically, carbon atoms comprised 62.5% and 71.0% for the pristine cotton wool and tissue paper, respectively. The binding energies of the detected atoms across all analysed samples are summarised in Table 7.1. In the modified samples, nitrogen peaks (N 1s) originating from the PVP

and PEI polymers were observed. Nitrogen atoms constituted 13.9% and 6.5% for coated cotton wool and tissue paper, respectively. This suggests that cotton wool is more effectively coated than tissue paper. However, upon closer examination of the SEM results, this discrepancy may be attributed to uneven coating in the samples. Moreover, carbon atom proportions increased in both samples, accounting for 78.6% in coated cotton wool and 80.7% in coated tissue paper, compared to their pristine counterparts. Consequently, in addition to SEM, XPS analysis further substantiates the coating of the materials.

Table 7.1 Binding energies of the detected elements of cotton and tissue paper.

Atom peaks	Binding Energy (eV)			
	Pristine-Cotton	Pristine-Tissue paper	PEI/PVP-Cotton	PEI/PVP-Tissue paper
C 1s	286.4	285.5	285.0	285.1
N 1s	-	-	399.0	399.7
O 1s	532.8	532.8	531.3	531.6

The carbon and nitrogen peaks of the samples underwent deconvolution to distinguish contributions from different chemical environments of each atom through high-resolution core-level analysis. As shown in Figure 7.4b,c, the C 1s spectra for pristine cotton wool and tissue paper revealed peaks related to C–C/C–H (284.6 and 284.7 eV), C–O (286.3 and 286.2 eV), C–O–C/O–C–O (287.7 and 287.8 eV) and O–C=O (288.5 and 288.5 eV), respectively. These are different chemical environments of the carbon atoms of the cellulose chemical structure of the cotton and tissue paper.^{15–17} In the case of the modified samples, the C 1s spectra exhibited changes, confirming the detection of new chemical environments. As illustrated in Figure 7.4d,e, the C 1s spectra of the modified samples were deconvoluted into four different chemical environments of the PVP structure (Figure 7.2).^{18–20} Additionally, the C–N and C–C/C–H constituents include contributions from similar chemical environments of the PEI. Notably, considering the observed uneven coating on the cotton fibres in the SEM images, it is plausible that the C–C=O peak may

also have contributions from the C–O–C/O–C–O within the cellulose structure. The N 1s spectrum of the modified cotton, presented in Figure 7.4f, displayed constituent peaks of N–H, N–C, and N–C=O, representing diverse nitrogen atoms’ chemical environments of PEI and PVP polymers. Similar constituents were observed for modified tissue paper. The binding energies of the various constituents within the C 1s and N 1s spectra of the coated samples are summarised in Table 7.2.

Table 7.2 Binding energies of different chemical environments of each core level.

C and N 1s	Binding Energy (eV)	
	PEI/PVP-Cotton	PEI/PVP-Tissue paper
C–C/C–H	284.4	284.5
C–N	285.1	284.9
C–C=O	285.9	285.3
C=O	287.9	287.6
N–H	398.7	398.5
N–C	398.9	398.8
N–C=O	401.2	401.1

As previously mentioned in section 7.3.1, the hydrophilic coating amplifies the surface energy of the treated substrates. However, this hypothesis is often not directly explored and is typically inferred qualitatively from measurements of underwater oil contact angles.²¹ To investigate this, IGC was employed to determine the surface energy of both cotton and tissue papers before and after surface modification through polymer coating. The γ_S^d component of surface energy was assessed using a series of alkanes ranging from C₆ to C₁₀. By analysing the elution behaviour of these probes, an alkane line was generated, enabling the determination of γ_S^d using the Schultz approach.²² The γ_S^{ab} was derived from the elution time and volume of polar probes, namely toluene and dichloromethane. The infinite dilution technique employed allows for

determination of the surface energy of the highest-energy active sites on the samples.²³ This is because in an infinite dilution, low concentration of probe molecules is used which can only cover high-energy active sites.

As depicted in Figure 7.5b, the determined γ_s^{ab} of the coated samples was higher compared to the pristine samples. This increase can be attributed to the rise in polar chemical groups on the coated samples originating from the PEI and PVP polymers. Particularly, the γ_s^{ab} of cotton increased by 69.7% after coating, rising from 5.9 to 10.0 mJ/m². Tissue paper exhibited a significant boost in γ_s^{ab} , increasing by 93.0% from 7.1 to 13.7 mJ/m² after modification. Notably, there was no significant change in the γ_s^d component of surface energy across the samples, suggesting that coating does not alter the Van der Waals interaction of the probes with the material surfaces. These findings confirm that indeed the coating enhances the surface energy of the materials, resulting in superwetting or superhydrophilic surfaces.

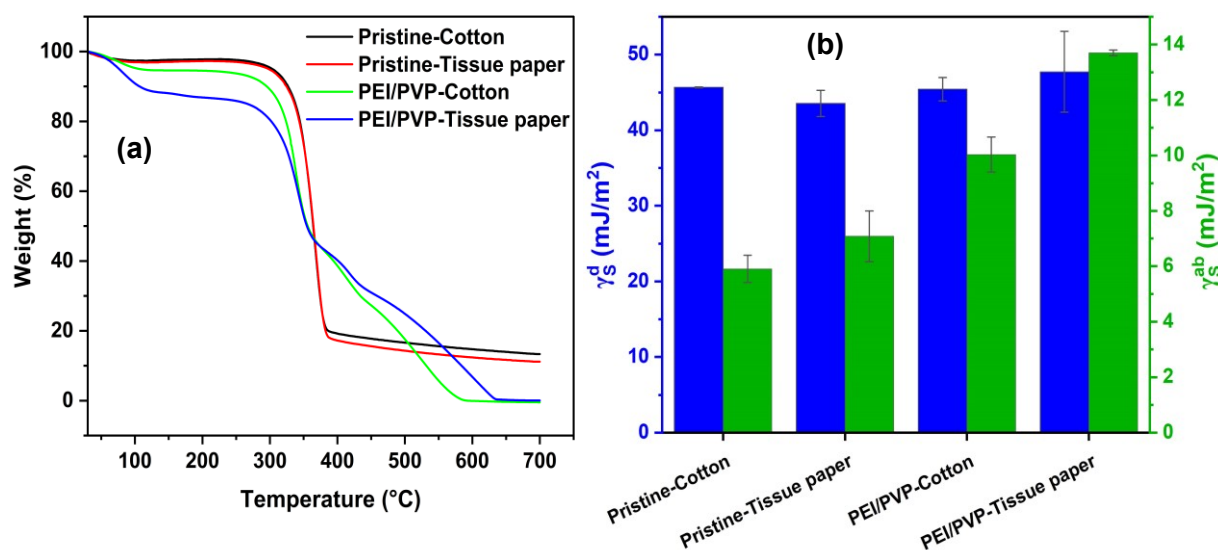


Figure 7.5 (a) TGA analysis and (b) surface energy of uncoated and coated tissue paper and cotton wool, respectively.

The thermal properties of the samples were evaluated under a nitrogen atmosphere using TGA analysis. As illustrated in Figure 7.5a, both pristine cotton and tissue paper exhibited similar thermograms with a pronounced major weight loss region (~97.0% to 19.7% and 17.8% for cotton and tissue paper, respectively) attributed to the pyrolysis of the cellulose structure, as previously discussed in Chapter 6. This significant decrease occurred within the temperature range of 280 to

390 °C. The residual weight losses of both pristine cotton and tissue paper at 700 °C were 13.3% and 11.1%, respectively. Additionally, pristine cotton and tissue paper displayed minor weight losses of 2.6% and 3.1% between 30 and 120 °C, attributed to the removal of moisture and volatile impurities in the samples. In contrast, modified samples exhibited weight losses (between 30 and 120 °C) of 5.3% and 11.1% for coated PEI/PVP-Cotton and PEI/PVP-Tissue paper, respectively. This elevated moisture content substantiates the superwetting surface properties of the coated samples. Notably, the pyrolysis of the coating and fibres commenced earlier at 260 °C compared to unmodified samples, a phenomenon observed in cellulose acetate and PEI matrices.²⁴ The decomposition of the modified samples after 200 °C occurred in two distinct regions. Firstly, a steep weight loss region between 260 and 365 °C, attributed to the pyrolysis of uncoated cellulose fibres, similar to the pattern observed in unmodified samples. Secondly, a slow, gradual weight loss region between 365 and 590 °C for coated cotton and 365 and 636 °C for coated tissue paper, indicative of the degradation of the coating polymers.^{24,25} Intriguingly, no weight loss was observed after the second region of weight loss, and surprisingly, the residual weight loss of the modified fibres was nearly zero. This implies that coated polymers enhance the combustion of cellulose fibres, raising potential safety concerns for the industrial application of these materials.

7.3.4. Separation of Surfactant-Stabilised Emulsion: Performance Evaluation of Modified Materials

The emulsion separation performance of four different coated substrates was assessed in a flow system under both gravity-assisted flow and an applied pressure setup. Owing to their superhydrophilic surfaces, the coating materials enable water to filter through while inhibiting oil permeation.^{7,10} Figure 7.6a illustrates the flux and separation efficiency achieved by each material under gravity-assisted separation. Uncoated materials exhibited poor separation efficiency ($\leq 8.5\%$) compared to modified samples. However, in terms of flux, pristine materials displayed slightly higher values. This is because the coating reduces the interstitial spaces of the fibres, as well as any pores in the tissue paper and tea bags. The coated cotton exhibited high flux (~ 800 L

$\text{m}^{-2} \text{h}^{-1}$), followed by tea leaves ($\sim 550 \text{ L m}^{-2} \text{h}^{-1}$), tea bags and tissue paper at 291 and 264 $\text{L m}^{-2} \text{h}^{-1}$, respectively. Coated cotton, tissue paper, and tea bags displayed significantly higher separation efficiency ($> 99.0\%$), indicating better coating of these materials.

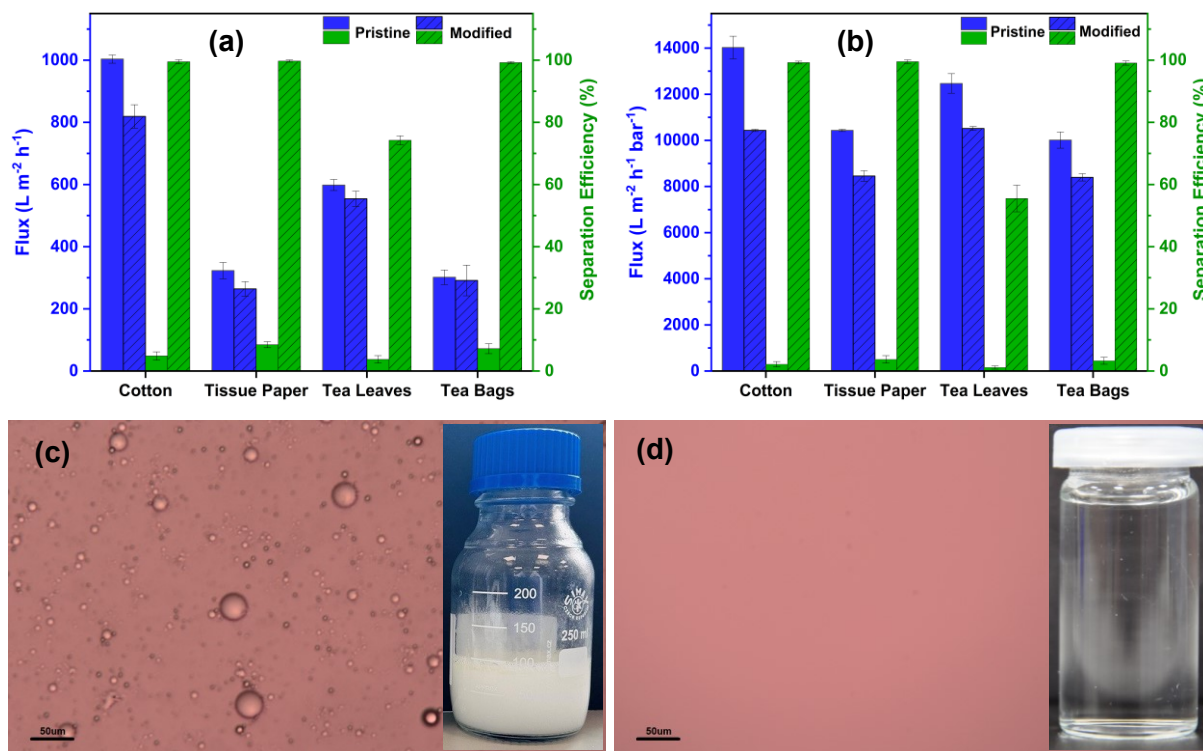


Figure 7.6 (a, b) Separation of surfactant-stabilised olive oil-in-water emulsion using different coated substrates using gravity assisted flow and applied pressure system, respectively. (c, d) Microscope images of the prepared emulsion and the filtrate after separation using coated cotton, respectively. The inserts show the photographs of the emulsion and the filtrate.

Similar efficiencies have been previously reported for PVP-coated cotton.⁷ Tea leaves showed a separation efficiency of 74.2%, still better than that exhibited by uncoated tea leaves. This also suggests better coating of the tea leaves but poor filtration due to larger voids in the packing. Even when compressed by the piston, unlike fibre substrates that compact together, tea leaves have solid particles that, upon packing, still have voids between them. These voids can lead to emulsion channelling during separation, resulting in lower separation efficiency.

Under the applied pressure system (Figure 7.6b), the flux increased by a factor of over 10. In this system as well, coated cotton, tissue paper, and tea bags maintained separation efficiency above 99.0%. However, individual separation efficiencies of these materials slightly decreased in this system compared to gravity-assisted flow. For example, coated cotton's separation efficiency

dropped from 99.5% in the gravity setup to 99.2% under the applied pressure separation. For tea leaves, there was a significant decrease in separation efficiency to 55.5%. The flux obtained in this study, under both gravity and pressure-assisted separations, is similar to those previously reported.¹⁰ However, some studies have reported significantly higher values.^{7,21} The oil concentrations in the filtrates are summarised in Table 7.3. For visualisation, photographs (inserts in Fig. 7.6c,d) of the emulsion and filtrate were taken for comparison, showing the emulsion changing from a white cloudy solution to clear filtrate after separation. Additionally, an optical microscope was used to image the prepared emulsion and the filtrate obtained after separation using modified cotton. As shown in Figure 7.6c,d, the image of the prepared emulsion displayed oil droplets in the continuous water phase, whereas in the clear filtrate, no oil droplets were detected.

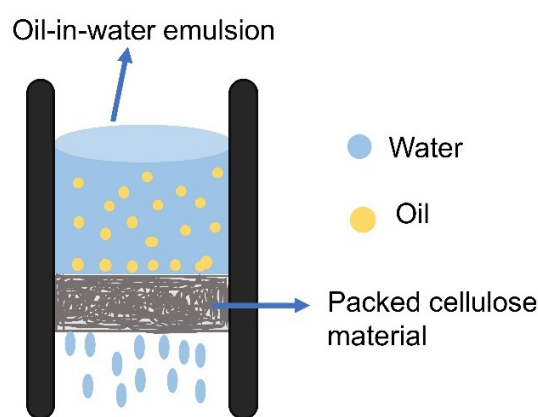


Figure 7.7 Schematic representation of oil-in-water emulsion separation.

The separation process is illustrated in Figure 7.7, where, as indicated, the continuous water phase easily permeates the compressed packed material. The oil droplets, owing to the underwater oil-repellent features and reduced pores/porosity of the packed filters, are effectively rejected.^{26,27} The initially rejected small oil microdroplets then commence coalescing and aggregating into larger particles, facilitating the demulsification of the emulsions.²⁶ In summary, the coated substrates are effective in emulsion separation, achieving very high separation efficiencies compared to the pristine samples. Therefore, these materials offer a potential solution to oils that end up in the sewer network due to ineffective emulsion separation by current existing technologies.

Table 7.3 Oil concentration in the filtrates.

Coated substrates	Oil in the filtrate (g/L)
Cotton wool	0.2
Tissue paper	0.1
Used tea bags	0.4
Used tea leaves	11.9

7.3.5. Separation of Surfactant-Stabilised and Surfactant-Free Emulsions, and Reusability Studies

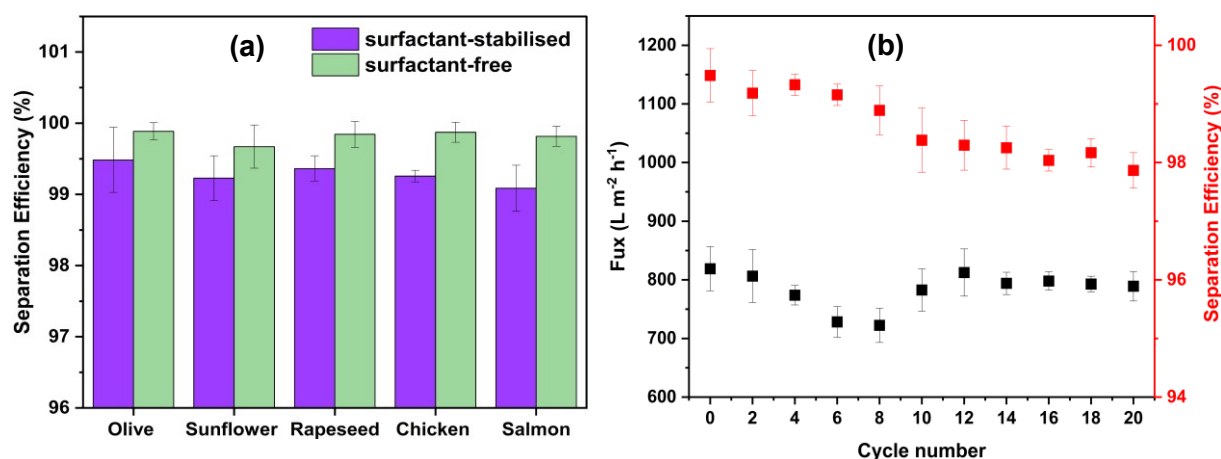


Figure 7.8 (a) Separation of surfactant-stabilised and surfactant-free oil-in-water emulsions made from different oils. (b) Recyclability test of the coated cotton using olive oil surfactant stabilised emulsion under gravity assisted.

Due to diverse dietary requirements and lifestyle choices, a variety of cooking oils are utilised in both domestic households and food service establishments. Consequently, it becomes crucial to develop materials that exhibit superior separation capabilities for any encountered emulsion. For the purposes of this investigation, modified cotton was exclusively employed. In Figure 7.8a, the separation of emulsions formed from cooking oils (olive, sunflower, rapeseed) and oils recovered from grilling salmon and chicken is presented. Notably, cotton demonstrated exceptional separation efficiency (> 99.0%) for these emulsions, both surfactant-stabilised and surfactant-free. Surfactant-free emulsions exhibited slightly higher separation, suggesting they are more readily separated compared to surfactant-stabilised ones. In an attempt to replicate oil-in-water emulsions found in the food industry, a surfactant-stabilised olive oil emulsion with NaCl (0.2 wt%), glucose

(0.1 wt%), and lysozyme (protein) (0.1 wt%) was prepared. This was undertaken to investigate the effects of other food components on emulsion separation. Surprisingly, no significant change in separation efficiency was observed, achieving 99.3% separation compared to 99.5% without the addition of other components.

The reusability of separation materials is a crucial attribute that enhances their superiority. The capability of modified cotton to be reused was investigated through 20 separation cycles (Figure 7.8b), employing a surfactant-stabilised olive oil emulsion and gravity-assisted flow. After each separation cycle, the packed bed underwent backflushing with ethanol twice and once with water. Modified cotton maintained a high separation efficiency ($\geq 99.2\%$) for the initial 6 cycles, gradually decreasing to a range between 99% and 98% from cycle 8 to 18. The separation efficiency recorded after cycle 20 was 97.9%. This decline in separation efficiency can be attributed to the gradual loss of coating over time since PVP is water-soluble. In terms of filtrate flux, there was a decrease from cycle 2 to 8 (from ~ 800 to $720 \text{ L m}^{-2} \text{ h}^{-1}$), followed by an increase in the flux back to approximately the initial level. This behaviour may be attributed to the clogging of interstitial spaces by any peeled coating during separation. It is important to note that the measured flux is an average for the separation time. Continuous build-up of oil on the top surface of the filter forms a barrier that increases resistance against filtration, causing the flux to decrease over time for the same separation cycle.⁷ Continuous washing after each cycle helps remove any clogging, resulting in an observed increase in flux. In summary, modified cotton exhibited robust separation performance after 20 cycles, demonstrating its potential for reuse and thereby reducing the manufacturing costs for industrial applications.

7.4. Conclusions

This study presented a straightforward and eco-friendly method for crafting superhydrophilic cellulose-based materials through the dip-coating of PEI/PVP polymers in a water. The prepared materials were then employed for separating oil-in-water emulsions, aiming to assess their effectiveness as a point source control solution for FOG deposits in sewers originating from

emulsions in various food-related industries and domestic households. Notably, modified cotton demonstrated higher separation efficiencies for various oils used in emulsions, whether surfactant-stabilised or surfactant-free. Furthermore, the modified cotton showcased impressive reusability, maintaining separation efficiencies above 97.0% even after 20 separation cycles. Overall, the findings of this study underscore the potential of superwetting materials for emulsion separation in food industries, serving as a preventive measure against FOGs entering sewer lines. Moreover, the method presented offers an economical and sustainable approach for producing superhydrophilic materials using recovered bio-waste materials.

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Chapter 8. Conclusions and Future Outlook

8.1. Conclusions

The aim of this project was to investigate sorption and filtration-based oil-water separation techniques as proactive solutions to recover FOGs from wastewater, aiming to prevent fatberg formation in sewers.

The efficacy of superhydrophobic powders in removing oils from water surfaces was successfully demonstrated. However, despite their effectiveness in oil-water separation, superhydrophobic powders displayed very low oil adsorption capacities (< 4.0 g/g). Additionally, the recovery of powders from oil-water mixtures post separation testing posed significant challenges, with some particles being lost. Furthermore, while the surface modification of powdered sorbents resulted in superhydrophobic surfaces, their reusability posed challenges due to the regeneration process involving washing in acetone and particle recovery via centrifugation. This method resulted in the loss of some particles with the supernatant. To address these limitations, the sorbents were scaled up using cotton wool in Chapter 5, employing a two-step sol-gel method to prepare superhydrophobic cotton wool. The findings of this study indicated a significant improvement in sorption capacities (> 37.0 g/g) compared to using powders alone. The prepared cotton was also effective in separating oily wastewater recovered from domestic household kitchens.

Chapter 6 introduced the use of a one-pot method to prepare superhydrophobic cotton wool, which was also effective in separating oils from water. The study further demonstrated the effectiveness of this cotton in separating surfactant-free oil-in-water emulsions, attaining over 90.0%. Additionally, the prepared superhydrophobic cotton wool sorbents by both two-step and one-pot methods were highly durable, maintaining their superhydrophobicity in different solvents, harsh acidic and basic solutions, as well as under laundering test conditions.

Chapter 7 illustrated the ease of separating oil-in-water emulsions using various superhydrophilic cellulose-based materials, including cotton, used tea leaves, used tea bags, and tissue paper. These substrates were dip-coated with hydrophilic PVP and PEI polymers to create superwetting materials, evident in their increased surface energy resulting from the introduction of high surface energy functional groups of the polymers. The modified cotton wool exhibited superior reusability, maintaining a separation efficiency of 97.9% after 20 reuse cycles, highlighting its practical potential.

In summary, this work presents a sustainable and environmentally friendly solution to the FOG deposit problem, offering an alternative FOG management strategy. The foundational knowledge provided here, along with future endeavours in scaling up and practical application, offers a promising avenue for best management practices.

8.2. Outlook

As sorption processes have been demonstrated to depend on the pore properties of materials, it will be crucial to utilise a large-scale substrate material with adjustable pores to investigate their effects on performance. Additionally, exploring the use of waste-based substrates can align the work with sustainability and circular economy goals. Some superhydrophobic materials have been shown to exhibit switchable wettability. It is important to explore methods to enable the superhydrophobic cotton fabricated in this research to have switchable wettability for separating emulsions using a filtration setup. One simple approach is to investigate the use of ethanol-water or acetone-water mixtures in various compositions to transition the superhydrophobic surface to a superhydrophilic state. In Chapter 4, it was demonstrated that the maximum adsorption capacity of silica nanoparticles decreased after modification. To understand this change, it is important to examine the surface area of the powders before and after modification and compare it to the observed adsorption capacity trends. Additionally, investigating the reduction of eggshell powder to the nanoscale to determine if this enhances its adsorption capacity is also essential.

While most of the investigations focused on two-component systems involving water and oil, it is essential to examine how cotton interacts with other food components. For instance, understanding the sorption of glucose, carbohydrates, proteins, etc., on cotton sorbents is necessary to assess their impacts during oil-water separation. Furthermore, employing more realistic oily wastewater from food processing industries will allow testing the efficacy of the prepared materials on industry-based FOG-rich wastewaters.

The continuous separation of emulsions in a packed column set requires investigation, as this is crucial for practical application of the materials. Although superhydrophobic cotton has proven effective in batch oil-in-water emulsion separation, studying the same property in a continuous flow system is vital. Additionally, examining the effects of packing the column with both superhydrophobic and superhydrophilic materials on emulsion separation efficiency is necessary. Exploring the sequence of packing, starting with either superhydrophobic or superhydrophilic materials, or incorporating more than two packing sections in the column, can provide valuable insights.

The voidage of the filter column's packing is a crucial factor that may have impacted the results in chapter 7. Therefore, it is essential to investigate this aspect, along with the influence of coating on the pores of cotton, tissue papers, and used tea bags, using imaging techniques such as Micro-CT scanning. Furthermore, it is important to explore the scale of both superhydrophilic and superhydrophobic materials to determine if their synthesis on a large scale will affect their performance. Additionally, the development of separator units using both materials should be explored, with the goal of translating this research into a practical application in a real-world setting.

Appendix

A.1. Supplementary Information for Chapter 5

A.1.1. Calibrations Curves

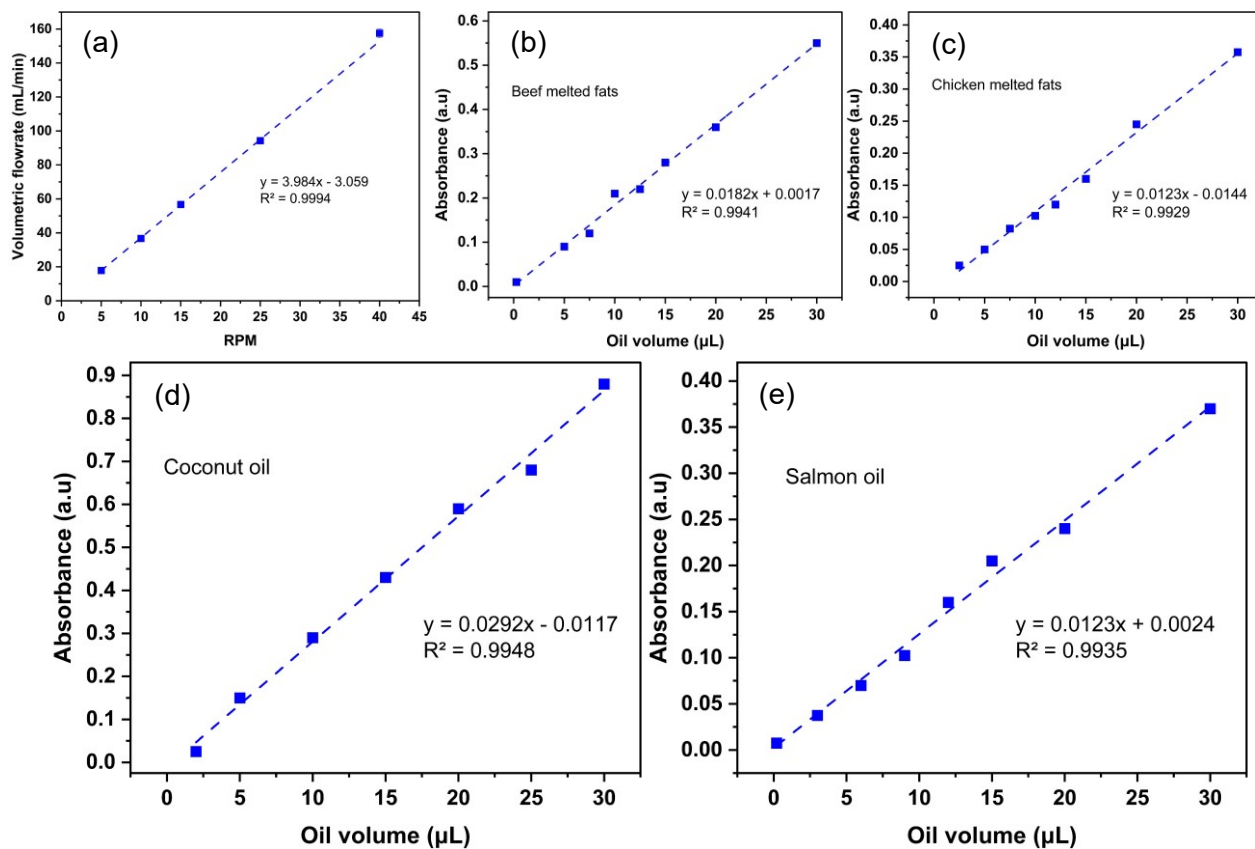


Figure A.1 Calibrations curves (a) pump flowrate, (b-e) oil concentration calibration, beef (b), chicken (c), coconut (d) and salmon oil (e).

A.1.2. SEM Images of A-C and N-C

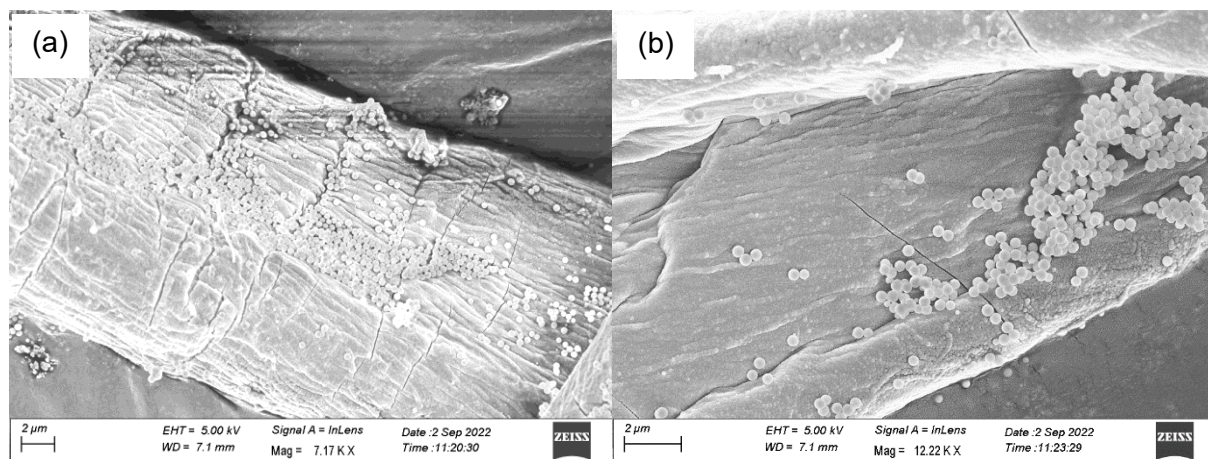


Figure A.2 (a,b) SEM images showing low silica nanoparticle loading in N-C and A-C cotton samples, respectively.

A.1.3. Images of Beef Tallow Fats, Solid and Semi-solid, Before and After Filtration

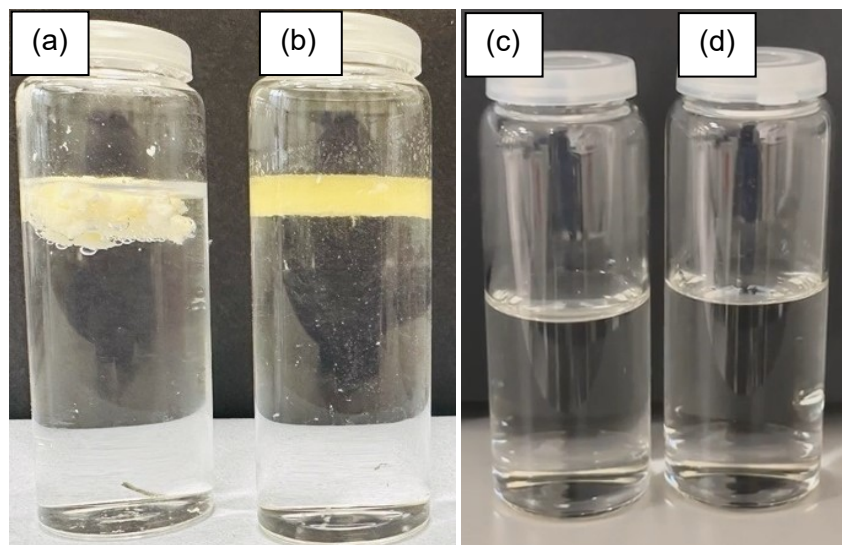


Figure A.3 (a, b) Images of beef tallow fat and congealed beef tallow fat- water mixtures, (c, d) clean water collected after filtration using raw cotton wool.

A.1. Supplementary Information for Chapter 6

A.2.1. High Resolution C 1s Spectra of Pre-treated Cotton

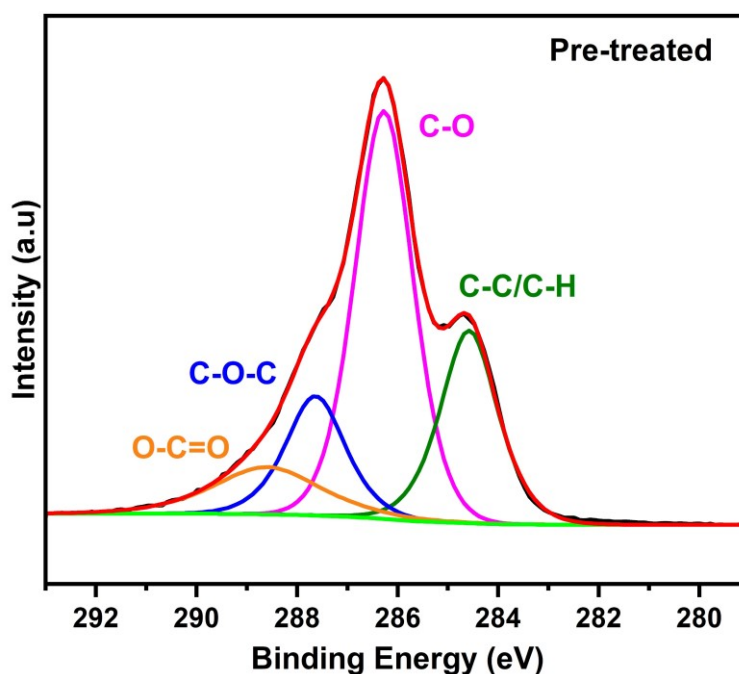


Figure A.4 C 1s spectra of pre-treated cotton.

A.2.2. Oil-water Separation



Figure A.5 Less stable oil-in-water emulsion separation.

The photograph of the emulsion, as depicted in Figure A.5, was taken 30 min after its preparation. As shown, the emulsion was already undergoing separation, with some oil gathering at the top of the glass vial.

A.2.3. Synthesis of Modified Cotton

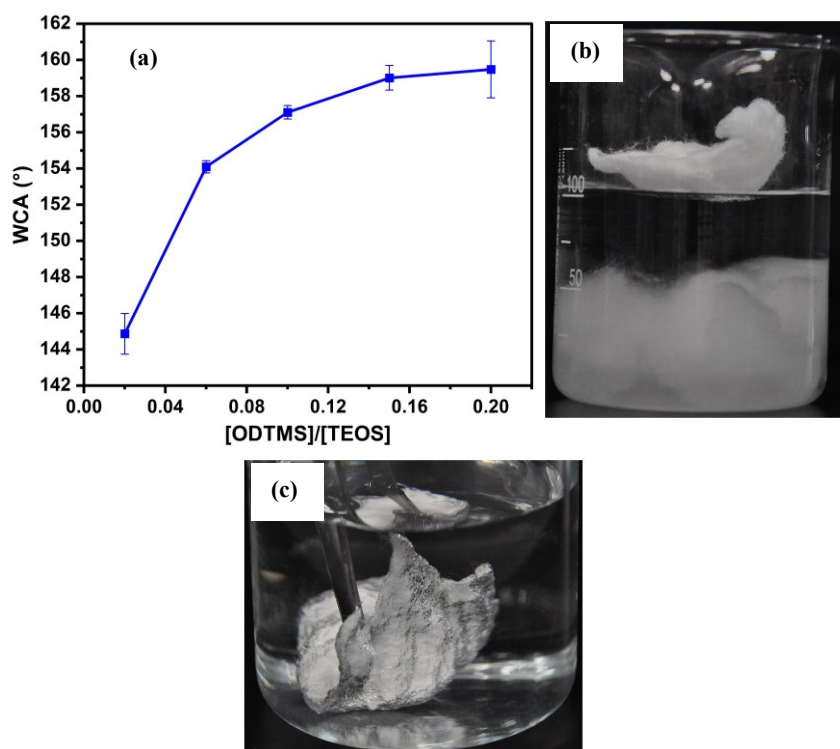


Figure A.6 (a) Effects of ODTMS concentration on hydrophobicity of cotton. (b, c) wettability of modified cotton.

The effects of ODTMS/TEOS ratio on the superhydrophobicity of the cotton were investigated by varying the amount of ODTMS. As shown in Figure A.6a, the contact angle decreased with ODTMS/TEOS the ratio. The superhydrophobicity was still achieved at low ODTMS/TEOS ratio (~ 0.06). Figure A.6b shows the comparison of modified and pristine cotton in water. The modified cotton floats whereas the pristine cotton soaks in water and sinks. In Figure A.6c, the modified cotton was intentionally submerged under water and it formed a light-reflective shiny coating around the cotton due to trapped air in the cotton.

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Table A.1 Summary of all the copyright permissions obtained to reproduce materials from the original works.

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29 & 30	Table	Table 2.1 & 2.2	Ref. No. 2: Properties influencing fat, oil, and grease deposit formation. (https://doi.org/10.2175/193864708X267441)	© 2008 Water Environment Federation	Mar 15, 2024	yes	1461784-1
29	Figure	Figure 2.1	Ref. No. 5: Fat, oil and grease deposits in sewers: Characterisation of deposits and formation mechanisms. (https://doi.org/10.1016/j.watres.2012.09.002)	© 2012 Elsevier Ltd.	Mar 11, 2024	yes	5745911508100
31	Figure	Figure 2.2	Ref. No. 12: Microbiologically induced corrosion of concrete in sewer structures: A review of the mechanisms and phenomena. (https://doi.org/10.1016/j.conbuildmat.2019.117813)	© 2019 Elsevier Ltd.	Mar 11, 2024	yes	5745940096610

33	Figure	Figure 2.3	Ref. No. 3: Mechanisms of Fat, Oil and Grease (FOG) deposit formation in sewer lines. (https://doi.org/10.1016/j.watres.2013.05.002)	© 2013 Elsevier Ltd.	Mar 10, 2024	yes	5745440209449
34	Figure	Figure 2.4	Ref. No. 16: Understanding the properties of fat, oil, and grease and their removal using grease interceptors. (https://doi.org/10.1016/j.watres.2022.119141)	© 2022 Elsevier Ltd.	Mar 10, 2024	yes	5745450308141
39	Figure	Figure 2.5	Ref. No. 48: Removal of Persistent Organic Pollutants (POPs) from water and wastewater by adsorption and electrocoagulation process. (https://doi.org/10.1016/j.gsd.2021.100575)	© 2021 Elsevier B.V.	Mar 10, 2024	yes	5745421489024
44	Figure	Figure 2.7	Ref. No. 40: Application of Efficient Magnetic Particles and Activated Carbon for Dye Removal from Wastewater. (https://doi.org/10.1021/acsomega.0c01905)	© 2020 American Chemical Society	Mar 11, 2024	yes	Permission confirmed by email (Open access)

46	Figure	Figure 2.8	Ref. No. 78: Preparation of surfactant templated nanoporous silica spherical particles by the Stöber method. Effect of solvent composition on the particle size. (https://doi.org/10.1007/s10853-007-1771-y) Ref. No. 75: Synthesis and surface functionalization of silica nanoparticles for nanomedicine. (https://doi.org/10.1016/j.surfrep.2014.07.001)	© Springer Science+Business Media, LLC 2007 © 2014 Elsevier B.V.	Mar 11, 2024 Mar 11, 2024	yes	5745890596160 5745890722043
50	Figure	Figure 2.9	Ref. No. 188: Superhydrophobic/superoleophilic cotton-oil absorbent: preparation and its application in oil/water separation. (https://doi.org/10.1039/C8RA05420G)	© The Royal Society of Chemistry 2018			(Open access)

52	Figure	Figure 2.10	Ref. No. 121: Environment-Friendly superhydrophobic sponge for highly efficient Oil/Water separation and microplastic removal. https://doi.org/10.1016/j.seppur.2023.124060	© 2023 Elsevier B.V.	Mar 13, 2024	yes	5747090206454
53	Figure	Figure 2.11	Ref. No. 130: Facile fabrication of superhydrophobic meshes with different water adhesion and their influence on oil/water separation. https://doi.org/10.1039/C6RA17153B	© The Royal Society of Chemistry 2016	Mar 15, 2024	yes	1461678-1
56	Figure	Figure 2.12	Ref. No. 159: Superhydrophobic MS@CuO@SA sponge for oil/water separation with excellent durability and reusability.	© 2021 Elsevier Ltd.	Mar 11, 2024	yes	5745861014642
57	Figure	Figure 2.13	Ref. No. 161: Fabrication of Durable Superhydrophobic Stainless Steel Mesh with Nano/Micro Flower-Like Morphologies for Self-Cleaning and Efficient Oil/Water Separation. https://doi.org/10.1007/s42235-022-00231-y	© The Author(s) 2022	Mar 14, 2024	yes	1461306-1 (Open access)

59	Figure	Figure 2.14	Ref. No. 161: Sprayed superamphiphilic copper foams for long term recoverable oil-water separation https://doi.org/10.1016/j.surfcoat.2017.11.068	© 2017 Elsevier B.V.	Mar 10, 2024	yes	5745591473439
60	Figure	Figure 2.15	Ref. No. 183: Preparation of novel cotton fabric composites with pH controlled switchable wettability for efficient water-in-oil and oil-in-water emulsions separation. https://doi.org/10.1007/s00339-018-1781-4	© Springer-Verlag GmbH Germany, part of Springer Nature 2018	Mar 10, 2024	yes	5745590187379