

Contents

| | |
|---|-----------|
| 1. Scope and outline of this thesis | 1 |
| 2. Literature review and fundamentals | 5 |
| 2.1. Responsive separation systems | 5 |
| 2.1.1. Microgel synthesis | 5 |
| 2.1.2. Properties of PNIPAM microgels | 8 |
| 2.1.3. Microgels at solid-liquid interfaces | 14 |
| 2.1.4. Gel membranes | 17 |
| 2.2. Enzymatically active separation systems | 23 |
| 2.2.1. Metal-organic frameworks | 23 |
| 2.2.2. Metal-organic frameworks in biocatalysis | 25 |
| 2.2.3. Supported metal-organic frameworks for application in membrane science | 31 |
| 2.2.4. Enzymatically active metal-organic framework membranes | 35 |
| 3. Materials and methods | 37 |
| 3.1. Microgel modified filtration systems | 37 |
| 3.1.1. Materials | 37 |
| 3.1.2. PNIPAM and PNIPAM- <i>co</i> -AAc core-shell microgels | 37 |
| 3.1.3. Dynamic light scattering | 39 |
| 3.1.4. Zetapotential | 39 |
| 3.1.5. Potentiometric titration | 40 |
| 3.1.6. Fabrication of microgel composite membranes | 40 |
| 3.1.7. Confocal laser scanning microscopy | 41 |
| 3.1.8. Field emission scanning electron microscopy | 42 |
| 3.1.9. Ellipsometry | 42 |
| 3.1.10. Microscopy study | 42 |

| | |
|---|-----------|
| 3.1.11. Pure water flux experiments | 43 |
| 3.1.12. Retention measurements | 45 |
| 3.2. Enzymatically active separation systems | 47 |
| 3.2.1. Materials | 47 |
| 3.2.2. Biomimetic mineralization of GOD@ZIF-8 | 47 |
| 3.2.3. Field emission scanning electron microscopy | 48 |
| 3.2.4. Enzymatic activity of GOD@ZIF-8 | 49 |
| 3.2.5. Encapsulation efficiency of GOD | 50 |
| 3.2.6. Trypsin and temperature stability | 50 |
| 3.2.7. Interfacial biomineralization of free-standing ZIF-8 and GOD@ZIF-8 films | 51 |
| 3.2.8. In situ growth of pepsin@ZIF-8 on cross-linked pepsin layers | 51 |
| 3.2.9. Fabrication of GOD@ZIF-8 films on hollow fiber membranes | 52 |
| 4. Monolayer microgel composite membranes with tunable permeability | 55 |
| 4.1. Introduction and motivation | 56 |
| 4.2. Results and discussion | 58 |
| 4.2.1. Synthesis of monolayer microgel composite membranes | 58 |
| 4.2.2. Formation of confluent microgel monolayers | 60 |
| 4.2.3. Reproducibility of microgel membrane preparation | 65 |
| 4.2.4. Stability of microgel composite membranes | 66 |
| 4.2.5. Responsiveness of the adsorbed microgel monolayer | 66 |
| 4.2.6. Support dependent MWCO study of microgel composite membranes | 68 |
| 4.3. Conclusions | 72 |

| | |
|--|-----------|
| 5. Charged microgels adsorbed on porous membranes | 75 |
| 5.1. Introduction and motivation | 76 |
| 5.2. Results and discussion | 78 |
| 5.2.1. Poly-(<i>N</i> -isopropyl-acrylamide)- <i>co</i> -acrylic acid microgels | 78 |
| 5.2.2. Microgel coating on membranes - The pore- covering concept | 80 |
| 5.2.3. Effect of AAc content and cross-flow velocity on the surface adhesion of microgels | 83 |
| 5.2.4. Microgel membrane interaction - a microscopy study | 85 |
| 5.2.5. Microgel coating of membranes - The pore- filling concept | 89 |
| 5.2.6. Retention of charged microgel membranes . . | 90 |
| 5.2.7. Stability of highly charged microgel membranes | 92 |
| 5.3. Conclusions | 95 |
| 6. MOF stabilized enzymatically active membranes | 97 |
| 6.1. Introduction and motivation | 98 |
| 6.2. Results and discussion | 100 |
| 6.2.1. Morphology and activity of GOD@ZIF-8 in sus- pension | 100 |
| 6.2.2. Temperature stability of GOD@ZIF-8 in sus- pension | 105 |
| 6.2.3. Trypsin stability of GOD@ZIF-8 in suspension | 107 |
| 6.2.4. Concepts for the generation of GOD@ZIF-8 membranes | 110 |
| 6.2.5. In situ biomineralization at the phase interface | 114 |
| 6.2.6. Morphology and activity of GOD@ZIF-8 mem- branes | 117 |
| 6.2.7. Conclusions | 122 |

Contents

| | |
|---|------------|
| 7. Reflection and outlook | 123 |
| A. Appendix | 127 |
| A.1. More details on monolayer microgel composite membranes | 127 |
| A.1.1. Characterization of PNIPAM core-shell microgels | 127 |
| A.1.2. Stability of microgel composite membranes | 128 |
| A.1.3. Support dependent MWCO study of microgel composite membranes | 129 |
| A.2. More details on charged microgels adsorbed on porous membranes | 130 |
| A.2.1. Cross-flow set-up | 130 |
| A.2.2. Reliability of zeta potential measurements | 130 |
| A.2.3. Potentiometric titration | 131 |
| A.3. More details on MOF stabilized enzymatically active membranes | 133 |
| A.3.1. Influence of synthesis parameters | 133 |
| A.3.2. Temperature and protease stability of GOD@ZIF-8 crystals in suspension | 134 |
| A.3.3. Localization of enzyme within the crystals | 136 |
| A.3.4. GOD stability in an 1-octanol/PBS emulsion | 137 |
| Bibliography | 138 |