
CONTENT OF THE THESIS

| Content | Page No. |
|-----------------------------------|---------------------|
| Abstract | i |
| Keywords | i |
| Declaration | iii |
| Certificate of Supervisor | iv |
| Certificate of Examiner | v |
| Preface | vi |
| Acknowledgement | vii |
| Contents of the Thesis | ix |
| List of Abbreviations and Symbols | xviii |
| List of Schemes | xxi |
| List of Figures | xxii |
| List of Tables | xxix |

Chapter 1

General Introduction

| | |
|----------------------------------|------|
| Highlights | 1-1 |
| 1.1. Introduction | 1-2 |
| 1.2. Historical background | 1-4 |
| 1.3. Classification of hydrogels | 1-5 |
| 1.4. Materials and methods | 1-7 |
| 1.4.1. Materials | 1-7 |
| 1.4.1.1. Polysaccharides | 1-8 |
| 1.4.1.2. Hydrophilic monomers | 1-13 |
| 1.4.1.3. Hydrophobic monomers | 1-14 |
| 1.4.1.4. Hydrophilic polymers | 1-15 |
| 1.4.1.5. Initiators | 1-16 |
| 1.4.1.6. Cross-linkers | 1-16 |
| 1.4.2. Methods | 1-19 |

| | | |
|----------|---|------|
| 1.4.2.1. | Physical cross-linking methods | 1-20 |
| 1.4.2.2. | Chemical synthesis methods | 1-22 |
| 1.5. | Characterization | 1-26 |
| 1.5.1. | Spectroscopic techniques | 1-26 |
| 1.5.1.1. | Fourier transform infrared (FTIR) spectroscopy | 1-26 |
| 1.5.1.2. | Ultraviolet-visible (UV-vis) spectroscopy | 1-27 |
| 1.5.1.3. | X-ray photoelectron (XPS) spectroscopy | 1-27 |
| 1.5.2. | Microscopic techniques | 1-27 |
| 1.5.2.1. | Inverted microscopy (IM) | 1-27 |
| 1.5.2.2. | Scanning electron microscopy (SEM) | 1-28 |
| 1.5.2.3. | Field emission scanning electron microscopy (FESEM) | 1-28 |
| 1.5.3. | Other techniques | 1-28 |
| 1.5.3.1. | Thermogravimetric analysis (TGA) | 1-28 |
| 1.5.3.2. | Differential scanning calorimetry (DSC) | 1-29 |
| 1.6. | Testing methods | 1-29 |
| 1.6.1. | Swelling ability | 1-29 |
| 1.6.2. | Mechanical testing methods | 1-29 |
| 1.6.3. | Biological testing methods | 1-29 |
| 1.6.3.1. | Cytotoxicity study | 1-29 |
| 1.6.3.2. | Antibacterial test | 1-30 |
| 1.6.4. | Biodegradation test | 1-30 |
| 1.7. | Property | 1-30 |
| 1.7.1. | Swelling | 1-30 |
| 1.7.1.1. | Deswelling and reswelling ability | 1-32 |
| 1.7.1.2. | Saline sensitivity | 1-32 |
| 1.7.1.3. | pH sensitivity | 1-32 |
| 1.7.2. | Cross-linking | 1-32 |
| 1.7.3. | Biocompatibility | 1-33 |
| 1.7.4. | Biodegradability | 1-33 |
| 1.7.5. | Mechanical property | 1-34 |
| 1.7.6. | Shape memory property | 1-35 |
| 1.7.7. | Self-healing ability | 1-35 |
| 1.8. | Applications | 1-36 |

| | | |
|----------|--|------|
| 1.8.1. | Biomedical fields | 1-36 |
| 1.8.1.1. | Controlled release of therapeutic agents | 1-36 |
| 1.8.1.2. | Tissue engineering | 1-36 |
| 1.8.1.3. | Wound dressing | 1-37 |
| 1.8.1.4. | Contact lenses | 1-37 |
| 1.8.2. | Wastewater treatment | 1-38 |
| 1.8.3. | Agricultural field | 1-38 |
| 1.8.4. | Miscellaneous applications | 1-38 |
| 1.9. | Scopes and objectives of the present investigation | 1-39 |
| 1.10 | Plan of research | 1-40 |
| | References | 1-40 |

Chapter 2

Starch-based superabsorbent hydrogel: Synthesis, characterization and properties evaluation in agricultural field

| | |
|---|-----|
| Highlights | 2-1 |
| 2.1. Introduction | 2-2 |
| 2.2. Experimental | 2-3 |
| 2.2.1. Materials | 2-3 |
| 2.2.2. Methods | 2-4 |
| 2.2.2.1. Synthesis of the superabsorbent hydrogel (SAH) | 2-4 |
| 2.2.2.2. Preparation of urea-encapsulated hydrogel | 2-5 |
| 2.2.3. Structural analysis | 2-5 |
| 2.2.4. Thermal study | 2-6 |
| 2.2.5. Swelling test | 2-6 |
| 2.2.5.1 Study of effect of cross-linker, initiator, and composition on swelling | 2-6 |
| 2.2.6. Biodegradation of the synthesized hydrogel | 2-6 |
| 2.2.7. Water-absorption capacity of soil | 2-7 |
| 2.2.8. Determination of density and porosity of the treated soil | 2-7 |
| 2.2.9. Study of urea-released profile | 2-7 |
| 2.3. Results and discussion | 2-8 |

| | | |
|----------|---|------|
| 2.3.1. | Synthesis of the SAH | 2-8 |
| 2.3.2. | Structural analysis | 2-9 |
| 2.3.2.1. | FTIR study | 2-9 |
| 2.3.2.2. | XPS study | 2-10 |
| 2.3.3. | Thermal degradation study | 2-11 |
| 2.3.4. | Swelling study | 2-12 |
| 2.3.4.1. | Effect of cross-linker on swelling | 2-13 |
| 2.3.4.2. | Effect of initiator on swelling | 2-14 |
| 2.3.4.3. | Swelling mechanism of SAH | 2-15 |
| 2.3.4.4. | Effect of salt | 2-16 |
| 2.3.5. | Biodegradation by soil burial method | 2-16 |
| 2.3.6. | Determination of water-holding capacity of soil | 2-17 |
| 2.3.7. | Determination of the density and the porosity of the soil | 2-17 |
| 2.3.8. | Controlled release of urea | 2-19 |
| 2.4. | Conclusion | 2-19 |
| | References | 2-20 |

Chapter 3

Starch-based double cross-linked amphoteric hydrogel: Synthesis, characterization and its dye adsorption study

| | | |
|------------|---|-----|
| Highlights | 3-1 | |
| 3.1. | Introduction | 3-2 |
| 3.2. | Experimental | 3-3 |
| 3.2.1. | Materials | 3-3 |
| 3.2.2. | Methods | 3-3 |
| 3.2.2.1. | Synthesis of the amphoteric hydrogel | 3-3 |
| 3.2.3. | Structural analysis | 3-4 |
| 3.2.4. | Swelling test | 3-4 |
| 3.2.5. | Dye adsorption study | 3-5 |
| 3.2.5.1. | Field emission scanning electron microscopy (FESEM) | 3-5 |
| | Study after dye adsorption | |
| 3.3. | Results and discussion | 3-5 |

| | | |
|----------|-------------------------------------|------|
| 3.3.1. | Synthesis of the hydrogel | 3-5 |
| 3.3.2. | Structural analysis | 3-6 |
| 3.3.2.1. | FTIR analysis | 3-6 |
| 3.3.2.2. | XPS analysis | 3-7 |
| 3.3.3. | Swelling of SETAs | 3-9 |
| 3.3.4. | Dye adsorption | 3-9 |
| 3.3.4.1. | Effect of adsorbent dosages | 3-10 |
| 3.3.4.2. | Effect of initial dye concentration | 3-11 |
| 3.3.4.3. | Effect of temperature | 3-12 |
| 3.3.4.4. | Effect of pH | 3-12 |
| 3.3.4.5. | Effect of contact time | 3-13 |
| 3.3.4.6. | Kinetics of adsorption | 3-14 |
| 3.3.4.7. | Isotherm study | 3-17 |
| 3.3.4.8. | Dye adsorption in a mixed system | 3-18 |
| 3.3.4.9. | Dye adsorption mechanism | 3-19 |
| 3.4. | Conclusion | 3-21 |
| | References | 3-22 |

Chapter 4

Starch-based mechanically tough hydrogel for effective removal of toxic metal ions

| | | |
|------------|--|-----|
| Highlights | 4-1 | |
| 4.1. | Introduction | 4-2 |
| 4.2. | Experimental | 4-3 |
| 4.2.1. | Materials | 4-3 |
| 4.2.2. | Methods | 4-3 |
| 4.2.2.1. | Synthesis of the mechanically tough hydrogel | 4-3 |
| 4.2.3. | Structural analysis | 4-4 |
| 4.2.4. | Determination of mechanical properties | 4-4 |
| 4.2.5. | Swelling study | 4-5 |
| 4.2.6. | Metal ion adsorption study | 4-5 |
| 4.3. | Results and discussion | 4-6 |
| 4.3.1. | Synthesis of the mechanically tough hydrogel | 4-6 |

| | | |
|--------|---|------|
| 4.3.2. | Structural analysis | 4-7 |
| | 4.3.2.1. FTIR spectral study | 4-7 |
| | 4.3.2.2. XPS study | 4-8 |
| 4.3.3. | Mechanical properties | 4-9 |
| 4.3.4. | Swelling study | 4-10 |
| 4.3.5. | Metal ion adsorption study | 4-11 |
| | 4.3.5.1. Effect of adsorbent dosages | 4-11 |
| | 4.3.5.2. Effect of pH | 4-12 |
| | 4.3.5.3. Effect of temperature | 4-13 |
| | 4.3.5.4. Effect of contact time | 4-13 |
| | 4.3.5.5. Effect of initial metal ion concentration | 4-14 |
| | 4.3.5.6. Kinetics of adsorption | 4-14 |
| | 4.3.5.7. Isotherm study of adsorption | 4-16 |
| | 4.3.5.8. Metal ions adsorption-desorption studies | 4-18 |
| | 4.3.5.9. Study on Cr (VI) adsorption | 4-18 |
| | 4.3.5.10. Treatment of actual industrial wastewater | 4-20 |
| | 4.3.5.11. Metal ion adsorption mechanism | 4-20 |
| 4.4. | Conclusion | 4-23 |
| | References | 4-24 |

Chapter 5

Starch-based physically cross-linked self-healing hydrogel

| | | |
|-------------------|---|-----|
| Highlights | 5-1 | |
| 5.1. Introduction | 5-2 | |
| 5.2. Experimental | 5-3 | |
| | 5.2.1. Materials | 5-3 |
| | 5.2.2. Methods | 5-4 |
| | 5.2.2.1. Synthesis of the self-healing hydrogel | 5-4 |
| | 5.2.3. Structural analysis | 5-4 |
| | 5.2.4. Determination of thermal properties | 5-5 |
| | 5.2.5. Determination of mechanical properties | 5-5 |
| | 5.2.6. Compression study | 5-5 |
| | 5.2.7. Impact resistance study | 5-5 |

| | | |
|--------|--|------|
| 5.2.8. | Swelling study | 5-5 |
| 5.2.9. | Determination of self-healing ability | 5-5 |
| 5.3. | Results and discussion | 5-6 |
| 5.3.1. | Synthesis of the self-healing hydrogel | 5-6 |
| 5.3.2. | FTIR spectral study | 5-7 |
| 5.3.3. | Thermal properties | 5-8 |
| 5.3.4. | Mechanical properties | 5-9 |
| 5.3.5. | Compression study | 5-11 |
| 5.3.6. | Impact resistance study | 5-12 |
| 5.3.7. | Swelling of the hydrogel | 5-12 |
| 5.3.8. | Self-healing ability | 5-13 |
| 5.3.9. | Toughening and self-healing mechanism | 5-15 |
| 5.3.10 | Comparison of present self-healing hydrogel with other reported . Hydrogels | 5-18 |
| 5.4. | Conclusion | 5-19 |
| | References | 5-20 |

Chapter 6

Fully bio-based hydrogels for biomedical applications with controlled drug release attribute

| | |
|------------|-----|
| Highlights | 6-1 |
|------------|-----|

Chapter 6A. Self-cross-linked starch/chitosan hydrogel as a biocompatible pH sensitive drug release system

| | | |
|-----------|--|-----|
| 6A.1. | Introduction | 6-2 |
| 6A.2. | Experimental | 6-3 |
| 6A.2.1. | Materials | 6-3 |
| 6A.2.2. | Methods | 6-4 |
| 6A.2.2.1. | Synthesis of the self-cross-linking hydrogel | 6-4 |
| 6A.2.3. | Structural analysis | 6-4 |
| 6A.2.4. | Thermal analysis | 6-5 |
| 6A.2.5. | Rheological measurements | 6-5 |
| 6A.2.6. | Swelling test | 6-5 |
| 6A.2.7. | Drug loading in hydrogel | 6-5 |

| | | |
|-----------|---|------|
| 6A.2.8. | Drug release study | 6-5 |
| 6A.2.9. | In vitro antimicrobial analysis | 6-6 |
| 6A.2.10. | Cytotoxicity analysis of OSC3 on human embryonic kidney cells (HEK 293) | 6-6 |
| 6A.2.11 | Biodegradation | 6-7 |
| 6A.3. | Results and discussion | 6-7 |
| 6A.3.1. | Synthesis of the hydrogel | 6-7 |
| 6A.3.2. | Structural analysis | 6-9 |
| 6A.3.2.1. | FTIR spectral study | 6-9 |
| 6A.3.2.2. | XPS analysis | 6-11 |
| 6A.3.3. | TGA analysis | 6-12 |
| 6A.3.4. | Rheological study of the hydrogel | 6-13 |
| 6A.3.5. | Swelling ability | 6-15 |
| 6A.3.6. | Encapsulation efficiency | 6-16 |
| 6A.3.7. | In vitro drug release | 6-16 |
| 6A.3.7.1. | Effect of pH on drug release | 6-17 |
| 6A.3.7.2. | Drug release kinetics | 6-19 |
| 6A.3.8. | Antibacterial study | 6-21 |
| 6A.3.9. | Cytotoxicity (cell compatibility) assay | 6-22 |
| 6A.3.10. | Biodegradation | 6-23 |
| 6A.4. | Conclusion | 6-24 |

Chapter 6B. Swelling induced mechanically tough starch/agar-based hydrogel for wound dressing applications

| | | |
|-----------|---|------|
| 6B.1. | Introduction | 6-26 |
| 6B.2. | Experimental | 6-27 |
| 6B.2.1. | Materials | 6-27 |
| 6B.2.2. | Methods | 6-27 |
| 6B.2.2.1. | Synthesis of the starch-agar-based hydrogel | 6-27 |
| 6B.2.3. | Structural analysis | 6-28 |
| 6B.2.4. | Thermal study | 6-28 |
| 6B.2.5. | Mechanical study | 6-28 |
| 6B.2.6. | Swelling study | 6-28 |

| | | |
|----------|--|------|
| 6B.2.7. | Water vapor transmission rate (WVTR) | 6-29 |
| 6B.2.8. | Drug loading | 6-29 |
| 6B.2.9. | In vitro drug release study | 6-29 |
| 6B.2.10. | Antimicrobial testing of the drug loaded hydrogel | 6-30 |
| 6B.2.11. | Cytotoxicity studies of the hydrogel on human embryonic kidney cells (HEK 293) | 6-30 |
| 6B.2.12. | Biodegradation via the soil burial | 6-30 |
| 6B.3. | Results and discussion | 6-30 |
| 6B.3.1. | Synthesis of the hydrogel | 6-30 |
| 6B.3.2. | FTIR study | 6-30 |
| 6B.3.3. | Thermal study | 6-32 |
| 6B.3.4. | Swelling study | 6-33 |
| 6B.3.5. | Water vapor transmission rate (WVTR) | 6-33 |
| 6B.3.6. | Mechanical properties | 6-34 |
| 6B.3.6.1 | Mechanical strength after swelling | 6-35 |
| 6B.3.7. | Drug loading and encapsulation efficiency | 6-36 |
| 6B.3.8. | Drug release | 6-37 |
| 6B.3.9. | Antibacterial activity | 6-39 |
| 6B.3.10. | Biocompatibility testing | 6-40 |
| 6B.3.11. | Biodegradation | 6-41 |
| 6B.4. | Conclusion | 6-42 |
| | References | 6-42 |

Chapter 7

Summary and future scopes

| | |
|-----------------------------|-----|
| Highlights | 7-1 |
| 7.1. Summary and conclusion | 7-2 |
| 7.2. Future scopes | 7-5 |

| | |
|-----------------------------|-----|
| List of Publications | a-b |
|-----------------------------|-----|