Summary and future scopes

Highlights

This chapter provides a concise and crisp summary of all the findings of the current investigation. The results are highlighted in a chapter-wise briefing with short concluding remarks to highlight the importance of the synthesized/fabricated materials. The chapter also addresses the future scopes offered by the present investigation for the enrichment of the ongoing hydrogel research.

7.1. Summary and conclusion

The thesis demonstrates the development of polysaccharide-based hydrogels with several special properties for multifaceted applications. The thesis is subdivided into seven chapters. The first chapter (**Chapter 1**) includes a general introduction to the polysaccharide-based hydrogels. Thereafter, the chapter presents a concise write-up on the structural architecture of the different moieties used for hydrogel preparation along with the synthetic procedures. A brief discussion on the different instrumentation techniques used for the characterization of hydrogel is also included. In the later sections, the special properties of hydrogels along with the potential applications in diverse fields are also highlighted. The chapter further provided the objectives, plans, and opportunities to execute the current research work.

The second chapter (**Chapter 2**) describes the synthesis, characterization, and property evaluation of starch-based superabsorbent hydrogel. The hydrogel was prepared by using starch and acrylic acid (AA) along with ammonium persulfate and *N, N*-methylene bis acrylamide (MBA) as the initiator and the cross-linker, respectively. Different compositions of hydrogels were synthesized to investigate the impact of monomer, cross-linker, and initiator on their water uptake abilities. The hydrogel with its high swelling ability utilized for the enhancement of the water-holding capacity of soil along with other soil properties such as bulk density and porosity. The hydrogel showed noteworthy encapsulation efficiency and controlled release ability of the agrochemicals like "urea" to reduce the leaching percentage when expose to water. In addition, the starch-based hydrogel showed profound biodegradability under soil burial conditions to specify it as a safe biomaterial for agricultural applications. All these results signify that the prepared hydrogel has immense possibilities for agricultural applications.

The third chapter (**Chapter 3**) of the thesis deals with the chemical modification of the hydrogel prepared in **Chapter 2**. The poly(acrylic acid) (PAA) chains provide only a negative charge and hence, in this work a double cross-linking strategy was utilized to incorporate both positive and negative charges to synthesize an amphoteric hydrogel. The first network of the hydrogel was prepared by epichlorohydrin (ECH) cross-linked starch, in which triethyl amine was reacted to incorporate a positive charge in it. The second network was prepared by PAA cross-linked by the cross-linker MBA. The formation of a double cross-linked network and the presence of quaternized alkyl chains reduce the swelling ability significantly. The hydrogel with both the cationic and anionic charges was applied for the removal of both acidic and basic dyes from the waste aqueous solution. Thus, this study paves a way for the fabrication of an efficient dye adsorbent for wastewater purification.

The fourth chapter (**Chapter 4**) describes the preparation of a starch-based mechanically strong hydrogel via the modification of the amphoteric hydrogel described in **Chapter 3**. In this work, MBA cross-linked PAA is grafted on the ECH cross-linked starch to achieve a double cross-linking strategy. To achieve the mechanically strong hydrogel, the dose amount of ECH was enhanced to introduce high cross-linking density with simultaneous removal of the positive charge formation step as mentioned in **Chapter 3**. The mechanical stability of the hydrogel was enhanced with an increase in the amount of ECH. Later the hydrogel was applied to remove toxic metal ions from the waste aqueous solution with pronounced efficiency. The high mechanical strength offers mechanical stability after metal ion adsorption and thus the hydrogel was easily removed from the aqueous solution without any secondary water pollution occurring from the breakdown adsorbent particles. Moreover, the hydrogel was a proficient recyclable adsorbent with several times recycle capability.

The fifth chapter (**Chapter 5**) deals with the preparation of a starch-based hydrogel with self-healing ability. The hydrogel was prepared via a micellar copolymerization technique by using both hydrophobic and hydrophilic monomers in the presence of a surfactant. The hydrogel can bear stress and automatically recombine the damaged zones without any external stimuli. Most importantly the inclusion of starch with the physically cross-linked hydrophobically associated network enhanced the mechanical strength of the hydrogel. In addition, the hydrogel can retain mechanical stability after water absorption and exhibit prominent tensile strength under swollen state. Thus, this work offers a starch-based mechanically tough hydrogel with a self-healing ability to enrich the hydrogel research.

The sixth chapter (**Chapter 6**) describes the preparation of a starch-based hydrogel for biomedical applications. Although the hydrogels described in **Chapter 2, Chapter 3, Chapter 4,** and **Chapter 5** are bio-based, but there are inclusion of synthetic monomers along with starch. Therefore, they are not suitable for biomedical applications. Thus, in this chapter, we aimed at the preparation of synthetic monomer-free hydrogels. The chapter is subdivided into two parts; the first sub-part (sub-**Chapter 6A**) described the synthesis of self-cross-linked hydrogel for an oral drug delivery system. To obtain this hydrogel, starch was oxidized to its dialdehydic derivatives. The carbonyl groups thus prepared react with the nearby hydroxyl groups of starch to form hemiacetal groups.

Moreover, the functionalized starch acts as a mono-cross-linker that reacts with an amine group containing polysaccharide, like chitosan via the formation of a Schiff-base. The presence of chitosan provides pH-responsive swelling ability as well as controlled release ability of ampicillin sodium salt drug. Most importantly, the noteworthy biocompatibility fulfills the most essential criteria to specify the hydrogel as a safe biomaterial in medicinal chemistry.

The second part of this chapter (sub-**Chapter 6B)** demonstrated the construction of a mechanically tough, synthetic monomer-free hydrogel for dressing applications. The hydrogel was synthesized by using the polysaccharides like 'starch' and 'agar', which were cross-linked with ECH. The hydrogel exhibited swelling-induced mechanical properties and the presence of agar is responsible for this unique property of the hydrogel. In addition to this, the hydrogel also exhibited prominent encapsulation efficiency for an antibacterial drug like Ciprofloxacin with controlled release ability. The encapsulated drug within the hydrogel can exhibit antibacterial ability. Most importantly the hydrogel was non-toxic for human embryonic kidney cells. Thus, the hydrogel acts as an efficient dressing material for advanced biomedical applications.

The present chapter, **Chapter 7,** provides concluding remarks on the significant findings of the current work. In addition to this, the future scopes of the present investigation are also highlighted.

The notable conclusions drawn from the current research work are summarized in the following section.

(i) The present study confirms that polysaccharide-based hydrogel can be synthesized by using various monomers, cross-linkers, and initiators with diverse properties and multiple-applicability.

(ii) Through proper selection of monomer, cross-linker, and polysaccharide, the properties of the hydrogels can be tuned along with imparting new properties like smart attributes.

(iii) This study showed that using a proper proportion of cross-linking density and initiator concentration a higher swelling ability can be attained with a lower monomer to polysaccharide ratio.

(iv) Amphoteric properties can be introduced with proper modifications for the removal of both cationic and anionic species from aqueous solution.

(v) The study shows that mechanically tough hydrogel can be prepared by using double cross-linking strategy in which one type of bond acts as a sacrificial bond to protect the whole hydrogel network.

(vi) Starch-based hydrogel with the smart properties like self-healing and mechanical stability even under swollen state can be prepared using proper modification and a suitable synthetic route.

(vii) Hydrogels suitable for biomedical applications can be prepared without the inclusion of any synthetic monomers. Oxidized starch can act as a macro-cross-linker to cross-link chitosan molecules. The presence of chitosan affects both swelling ability and controlled drug release ability which are highly sensitive to the solution pH.

(viii) The study showed that the introduction of a suitable polysaccharide can provide hydrogel with a unique attribute like swelling-induced mechanical stability without any synthetic monomers. Along with this property the hydrogel exhibited the noteworthy cell viability and controlled release ability for wound dressing application.

Thus, the present investigation illustrates the innovation of starch-based hydrogel with the desired properties. It can be seen that by changing the various monomers and cross-linkers, starch can be modified with multiple functionalities that are suitable for different advanced applications.

7.2. Future scopes

The thesis presents a comprehensive study on the development of starch-based hydrogels for various potential applications. Even though the current works offer several hydrogels with smart attributes, there are numerous opportunities open up for future research. Thus, based on the current findings future perspectives are given below.

(i) Completely bio-based hydrogel with higher swelling ability may be attempted.

(ii) Biocompatible hydrogel similar to living tissue can be attempted for tissue engineering scaffolds, bio-imaging, etc. applications.

(iii) The potential application of self-healing hydrogel can be attempted.

(iv) Extensive study may be carried out to design multipurpose hydrogels for the energy sector such as supercapacitors, fuel cells, electrocatalysis, metal-ion batteries, bioelectronics, etc.

(v) Nanotechnology can be applied along with the virgin hydrogel to modify various properties and to impart new properties for different advanced applications.

(vi) Fabrication of hydrogels with smart properties such as underwater healing, adhesive, etc. along with biocompatibility can be attempted.

(vii) In-vivo drug release study and investigation of the efficiency of the dressing material by using a suitable model can be attempted.