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Cellulose Hydrogels And Green Sustainable

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Abstract:

Cellulose is a highly abundant, green, sustainable, and biodegradable polymer. These characteristic features of cellulose make it a useful polymer for the synthesis of bio based hydrogel /or soft material for various applications. This article is focused on the preparation of biodegradable and biocompatible cellulose-based hydrogels using different methods based on the crosslinking agents used and the solvents used for cellulose dissolution. A study on the classification of different types of hydrogels was also reported. This article also discusses the self-healing cellulose-based hydrogel, bacterial cellulose-based hydrogel and includes the use of cellulose hydrogel in agriculture, biomedical field such as wound healing, wound dressing, and tissue engineering, water purification, removal of heavy metal, and in environmentally beneficial supercapacitors.

Introduction

On looking forward to the research of the 21st century, it has become clear that the use of renewable resources and natural polymers for mankind is the sole aim of scientists worldwide. The use of natural polymers like starch, cellulose, keratin, chitin, and gelatine in the research & development sector and commercial sector are widely explored to replace extensively used petroleum-based polymers. By combining both research & development and commercial approaches, it is realized that lignocellulosic biomass is one of the major natural and renewable

Cellulose cannot be used in its natural form like other polymers due to the rich in hydroxyl groups. It is modified with the help of several chemical reactions to form cellulose hydrogel [9]. Cellulose hydrogels are extensively cross-linked and hydrophilic polymers that are extended in three dimensions. Crosslinking strategy for the preparation of cellulose-based hydrogel is shown in Figure 2. These hydrogels are used in baby diapers and female hygienic products due to their excellent fluid absorbance ability without losing the actual shape [10]. The reason behind retaining the proper shape is the presence of weak (H-bonding, Ionic interactions, and Vander walls interactions) and strong interactions i.e., covalent bonds which held the hydrogel in its intact form. Thus, cellulose is merely not an agricultural or industrial waste but it is involved in a major proportion of our daily utility. In this review, we will discuss the preparation of cellulose hydrogels and their widespread applications based on their properties.

Hydrogel :

The hydrogel was first synthesized in the 1960s by Wichterle and Lim [11]. This is a miscellaneous mixture of two or more phases. The dispersed phase is water and the solid phase is a three-dimensional network [12-15]. Polysaccharide hydrogels are classified into various types based on (1) preparation method, (ii) types of monomer/polymer involved, and (iii) ionic charge. Based on the preparation method, polysaccharide hydrogels are classified into two subtypes: (a) physically (reversible) crosslinked hydrogels, and (b) chemically (permanent) crosslinked hydrogels [16].

Physically crosslinked hydrogels :

These are reversible and unstable hydrogels where monomers are connected by each other through weak interactions like hydrophobic interactions, ionic interactions, and intermolecular and intramolecular hydrogen bonding. Cellulose exhibits inter-, and intramolecular hydrogen bonding (Figure 3). Hydrophobic interactions are responsible for the dissolution of cellulose.

These hydrogels are frequently used in biomedical fields due to the absence of any external linking. Cellulose-polyvinyl alcohol hydrogel synthesized by the freeze-thaw process is an example of physically crosslinked hydrogel [17].

Chemically Crosslinked Hydrogels :

These are irreversible and more stable hydrogels than physically crosslinked hydrogels. The hydroxyl and carboxyl groups of cellulose are covalently linked to the amine, carboxyl group, and amide group of cross-linking agents. Cross-linking occurs by free radical polymerization, esterification, Michael Addition, etc (Figure 4). Citric acid, succinic acid, epichlorohydrin, and divinyl sulfone, etc. are usually employed as crosslinking [18].

Table : CELLULOSE HYDROGELS FOR HEAVY METAL REMOVAL

Material	**Preparation Method**	**Heavy Metal**	**pH**	**Temp (°C)**	**Ref.**
CMC/ECH	Chemical Cross Linking	Cu, Ni, Pb	7	RT	[47]
CMC-g-poly (NIP Am-co-AA) MMT	Chemical Cross Linking	Cu, Pb	4	RT	48
PVC/CMC	Freez-thaw	Ag, Ni, Cu, Zn	1.5	15	49
Chiltosan/PVA/GA	Chemical Cross Linking combined with Freeze-thaw	Hg, Cu, Cd, Pb	2.00 - 5.85	30	50
PVA+p(AAmNIP Am)	Chemical Cross Linking	Cu, Ni, Pb	6.0	2.5	5.1

Wound dressing :

Skin acts as the external barrier to various types of microorganisms. Minor cuts on the skin can be easily healed by the body and deep wounds can be further infected by microbes which could result in serious infection. Therefore, wound dressing soft materials having antibacterial properties is of great significance. Cellulose-based hydrogel exhibits water absorption properties and provides suitable moist conditions for wound healing. Antibiotic hydrogels can absorb tissue exudates and kill bacteria in wounds. Bacterial cellulose has high water uptake potential and high porosity. Hence this type of hydrogel can be used for the treatment of burn wounds/or as skin substitutestea and the main ingredient is Epigallocatechin-3-gallate (EGCG) which have anti inflammatory property. Studies have shown that KEC accelerates thrombin activation. and platelet aggregation which increases the haemostatic effect [55].

Controlled Drug delivery Conventional drug delivery (CDD) system has various disadvantages and the commonly practiced conventional method is the oral delivery method. These methods can immediately release the drug but do not maintain the adequate concentration of drug required for treatment. Controlled drug delivery has several advantages over CDD. However, controlled methods are used for maintaining the safe and effective release of drugs [56]. Natural hydrogels are employed in drug delivery because of their high water absorption, large porosity, and non-toxicity. Synthetic hydrogels avoided because of the toxic cross-connection agent in them. Natural pH-sensitive hydrogels are used for the delivery of protein drugs with 97.6% efficiency [57]. Diana Ciolacu et al.

prepared hydrogel from cellulose and lignin by cross-linking with epichlorohydrin (ECH) having high swelling properties. Lignin was incorporated for the regulated release of drugs [58]. Sultan Butun et al, synthesized carboxymethyl cellulose (CMC) hydrogel using divinyl sulfone as a cross-linking agent via single step using the reverse micelle microemulsion polymerization method. These hydrogels were further used for drug delivery due to their biodegradability and biocompatibility [59]. Acyclovir (Ac) is a herpes virus that was used for testing the controlled release of CMC particles. They also synthesized m-CMC particles which had higher release capacity. They further described that multistep drug loading increases release efficiency. Joachim E Arikibe et al. prepared bacterial cellulose/chitosan-based semi-interpenetrating hydrogels (semi-IPN) crosslinked with genipin. The synthesized hydrogel exhibited pH-responsive swelling properties and was used for drug release study. The swelling of the non-crosslinked hydrogels decreased with the increase of pH. Whereas, swelling of the crosslinked hydrogels increased as the chitosan ratio increased at low pH. It was reported that non crosslinked structure released drugs faster than cross-linked structure whereas cross linked structure release-controlled amount of drug [60].

Water purification

Various materials are available to remove soluble and insoluble pollutants and toxicants from the water by solid-phase extraction. Hydrogel is a soft material and exhibits good absorbency property and hence can be used for the purification of water. Cellulose hydrogel is an immerging soft material for water purification due to its biocompatibility, biodegradability, and non-toxicity. Pollutants enter into the network of cellulose hydrogels and are embedded inside the network through a different kinds of interaction (complexation with the lone pair or electrostatic attraction) with the amine or hydroxyl group of the hydrogel [61]. L. Zhang et al. reported cellulose/chitin hydrogel for Pb^{2+} adsorption. They described that complex formation between Pb^{2+} and N atom in the chitin was the key mechanism of Pb^{2} removal from solution. Moreover, the hydrophilic and microporous-network structure of cellulose hydrogel also played an important role in increasing adsorption ability [62]. L. Zhang et al. further reported chitin /cellulose blend membranes for efficient removing of heavy metal ions (Hg, Cu^{2}", and Pb^{2}") from aqueous solution. The uptake capacity of the heavy metal ions increased with the increase of chitin content. The adsorption of metal ions by chitin/cellulose composite was due to the complexation, electrostatic attraction, and metal chelation [63].

Cellulose hydrogel is an important soft material for tissue engineering in the biomedical field. These soft biomaterials are used as a scaffold to provide nutrients and space for new tissue formation such as skin, cartilage, bone, fat, muscle, neurons, artery, ligament, and liver. Moreover, the soft material should be biodegradable and have good cell adhesion properties. The addition of secondary components into the scaffold improves the material properties [64]. Sybele Saska et al. bacterial cellulose-collagen hydrogel for bone tissue engineering. They used glycine-modified bacterial cellulose, type I collagen, and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide as cross-linking agent for hydrogel synthesis. Collagen facilitates cell proliferation and enhances cell adhesion and function [65]. Pre-pre

Agricultural application :

Cellulose hydrogels are used in agriculture due to their superabsorbent property, eco friendly, biodegradability, and biocompatibility. Physical and chemical cross-linking structure imparts super absorbance property in the cellulose hydrogel. Although acrylate-based hydrogels are well-known superabsorbents; however, cellulose hydrogels are more promising as they are made from renewable polymer and biodegradable in nature. Whereas, acrylate-based hydrogels are a synthetic soft material and are not easily degradable [66]. C. Demitri et al. synthesized biodegradable cellulose hydrogel using carboxymethyl cellulose sodium salt and hydroxyethylcellulose. They used carbodiimide as a non-toxic cross-linker. The synthesized hydrogel was used in agriculture as a water reservoir where water scarcity is the major problem. Hydrogel releases the absorbed water without adding additional water from external sources. It also behaved as a soil conditioner which increases the physical and chemical quality of soil and also improves its fertility rate. There are two methods to load hydrogel With nanoparticles using cellulose composite hydrogels and used these to carry out Mizoroki Heck reaction for aryl halides with olefins. Polysaccharides (chitosan NPs and dialdehyde cellulose nanowhiskers) and graphene oxide nanosheets were used to prepare the hydrogel and used the same as a support to prepare palladium nanoparticles [74]. Ines Cunha et al. synthesized cellulose-based hydrogel electrolyte and used it as a gate dielectric in paper electrolyte-gated transistors. The hydrogel electrolyte film was synthesized by the dissolution of microcrystalline cellulose in an aqueous LiOH/urea solution followed by the addition of carboxymethyl cellulose. This film possesses unique features like flexibility, high capacitance, and transparency. Therefore, it is applicable as flexible electrical biosensors [75]. liances like electrolyte gated transistors or as

Conclusion :

Hydrogels are a promising material for application in drug delivery, wound dressing. tissue engineering, contact lenses, hygiene products, water purification, removal of heavy metal ions, supercapacitors, the agricultural sector (control release of fertilizer). Cellulose has several advantages such as high abundance, biocompatibility, biodegradability, and high mechanical strength. Due to these advantages, cellulose becomes a unique biopolymer for hydrogel synthesis. Cellulose hydrogel can be synthesized either from plant-based cellulose or from bacterial cellulose. However, due to the crystalline nano-fibrillar structure, bacterial cellulose hydrogel has several advantages over plant cellulose hydrogel. Cellulose is insoluble in water, hence various factors dissolution and derivatization of cellulose are two important factors for cellulose hydrogel synthesis. Cellulose hydrogel is mostly synthesized by dissolving cellulose is in NaOH/urea/H_2O or LiOH/urea/H_2O medium followed by the addition of cross-linker agent as epichlorohydrin (ECH). Both physical crosslinking and chemical crosslinking are utilized to prepare cellulose hydrogel. Cellulose hydrogel is an environmentally sustainable material and a promising alternate for the replacement of hazardous petroleum-based hydrogels

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