General Introduction

Highlights

This chapter presents a general introduction to superabsorbent hydrogels (SAHs). A brief review of the various hydrogels and their preparative methods including raw materials and reinforcing agents have been included in this chapter, with a particular emphasis on bioderived hydrogels as well as on the different nanomaterials incorporated SAH nanocomposites. Based on the literature reports, general methods for preparation of hydrogels and reinforcing agents, different instrumentation techniques used for their characterization, property evaluation and their applications in diverse fields are briefly addressed here. Further, the chapter includes scopes and objectives as well as plans to carry out the present research work.

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[1] Sarmah, D., Bora, A., and Karak, N. Hydrogel Nanocomposites Derived from Renewable Resources. In Pathania, D. and Singh, L., editors, *Bio renewable nanocomposite materials: For electrocatalyst, energy storage, and wastewater remediation*, Pages 269-285. American Chemical Society, 2022.

[2] Bora, A., Sarmah, D., and Karak, N. Hydrogels for environmental applications. In Aleman, C., Gupta, R., Garcia, J. M., editors, *Multifunctional hydrogels: From basic concepts to advanced applications,* CRC Press, 2023. *(Accepted)*

1.1. Introduction

Since the beginning of the 20th century, the development of polymer materials has played an important role in this growing world from an economic and industrial viewpoint. Among different engineering materials, polymers are fulfilling the needs of modern lifestyles through a variety of applications. Therefore, they are considered as the most useful materials for human society [1]. Moreover, a lot of research is still being carried out to promote the advancement of polymeric materials.

Among various polymeric materials, hydrogels have fascinated extensive interest because of their excellent properties as well as their wide applications in different fields. Hydrogels are three-dimensional (3D) cross-linked network structure that can swell significant amounts of water, saline solution, biological fluid, etc., even under certain pressure and gradually release them into the environment under exposure of various external stimuli [2]. They can be obtained via both chemical as well as physical cross-linking methods and can be synthesized in various forms such as beads, films, nanocomposites, etc. [3]. Currently, researchers from material science have been attracted to the development of superabsorbent hydrogels (SAHs) due to their enhanced water swelling capacity. They have higher water absorption capacity (WAC) as compared to common hydrogels and are capable of absorbing water up to 1,000-1,00,000 percent of its dry weight due to presence of additional hydrophilic groups such as amide (-$CONH_2$), amino (-NH_2), carboxyl (C=O), hydroxyl (-OH) and sulfonic (-SO_3H) groups on their polymeric backbones [4-6].

Based on the raw materials, SAHs are divided into two types, synthetic and biobased. Synthetic SAHs are prepared based on petroleum-based monomers such as acrylonitrile (AN), methacrylamide (MAM), acrylic acid (AA), etc. [7]. Due to extended service life, high water swelling, high processability, and availability of various raw chemical resources, synthetic hydrogels have drawn significant interest from different researchers. However, the use of conventional synthetic-based SAHs poses major risks to sustainability of the ecosystem. Therefore, biobased SAH has been considered as an interesting polymeric material to replace the conventional one. The biobased SAHs are mainly produced from polysaccharides and proteins such as alginate, cellulose, gelatin, guar gum, pectin, chitosan, starch, etc. along with grafting monomers such as AA, acrylamide (AM), itaconic acid (IA), etc. using different methods [8]. Their biodegradability strongly depends on the temperature, oxygen content, humidity, pH of

the solution, etc. [9]. Further, they exhibit biocompatible, and slow-release properties that make them suitable as controlled release fertilizer systems, soil conditioners, etc. for agricultural applications [10]. Besides, the presence of hydrophilic functional groups and their porous structure make them ideal candidates for adsorption of various water pollutants such as dyes, metal ions, pesticides, etc. from wastewater. Moreover, they have also been extensively utilized as drug delivery systems (DDS) due to their non-toxic, less severe side effects, excellent encapsulation efficiency, slow drug release properties, etc. over the decades. Additionally, they are employed in many other fields of applications including personal hygiene, biosensor, energy storage devices, etc. [11,12]

Although biobased SAHs have many applications due to their excellent properties, they are far away from achieving the same properties as conventional synthetic hydrogels. Therefore, modern research has focused on the fabrication of SAH composites (SAHCs) and SAH nanocomposites (SAHNCs) by incorporating different micro- and nano-sized reinforcing materials, respectively into the matrices to obtain hydrogels with radiant characteristics such as high porosity, multifunctionality, high surface area, improved WAC, etc. In the case of SAHCs, different micro-sized materials such as cellulosic materials and clays (montmorillonite (MMT), bentonite (BNT), etc.) are incorporated, while different nanomaterials (NMs) such as metal/metal oxides (Ag, TiO_2, ZnO, Fe_3O_4, etc.), graphene oxide (GO), cellulosic NMs (cellulose nanofiber (CNF), cellulose nanowhisker (CNW), etc.) are incorporated to impart the hydrogels with various outstanding properties [13,14]. Further, metal and cellulosic NM-based nanohybrids fabricated via electrostatic assembly are also used as reinforcing agents. The addition of these micro-reinforcing agents as well as NMs enhanced the properties of native hydrogels without affecting their intrinsic properties [15]. Therefore, to fulfill the growing needs of industrial-scale applications, significant attention has been devoted to the successful design and subsequent applications of biobased SAHs, SAHCs and SAHNCs.

1.2. Historical background

Over the past decades, researchers have developed hydrogels from inert matrices to smart materials. The term “hydrogel” was first used in 1894, when it was used to designate colloidal gels produced from certain inorganic salts [16]. Nowadays, the term is used to indicate an entirely different class of material. They are defined as 3D cross-linked polymeric materials that are capable of absorbing a huge volume of water without

disintegrating. In 1949, poly(vinyl alcohol) (PVA) and formaldehyde-based hydrogel appeared on the market for the first time and were used for biomedical implants [17]. However, the synthesis of poly(2-hydroxyethyl methacrylate) (poly(HEMA)) gels for contact lens application in 1960, was the real turning point for the hydrogels, which signified the initial point for a widespread and growing hydrogel market [18]. In particular, they have shown widespread applications in drug delivery, baby diapers, soft contact lenses, solid air fresheners, tissue engineering, bio adsorbent, separation systems, etc. In 1970, the US Department of Agriculture developed the first superabsorbent polymer (SAP) by applying alkaline treatment to starch-graft-poly(acrylonitrile) (PAN) at the Northern Regional Research Laboratory. However, insufficient gel strength and cost were the major disadvantages of the polymer. Thereafter, Japan first commercially produced SAP in 1978 for use in female napkins. Thereafter, France and Germany utilized SAP for making baby diapers in 1980 [19].

Since 1980, research on hydrogels has shifted from simple synthesis to the development of so called "smart hydrogel" with excellent properties such as external stimuli responsive, self-healing, mechanically tough, etc. Hoffman *et al*. first developed a dual (pH and temperature) responsive hydrogel in 1992 with the purpose of amylase release [20]. The hydrogel was prepared using AA, N-isopropyl acrylamide (NIPAM), divinyl silicone rubber in presence of some amount of cross-linker. Thereafter, self-assembled hydrogels based on polysaccharides and peptides were explored for fabrication of hydrogels with an ordered structure. In 1994, Li *et al.* developed a cyclodextrin-based self-assembled hydrogel for the first time [21].

However, conventional hydrogels have suffered from low physical and mechanical properties. Therefore, to obtain hydrogels with enhanced properties, different forms of hydrogels have been prepared, such as double network hydrogels, hydrophobically associated hydrogels, hydrogel nanocomposites (HNCs), etc. In particular, HNCs have drawn considerable attention due to their simple synthesis process as well as their unique properties. They are prepared via various physical and chemical cross-linking methods with the incorporation of NM into synthetic or natural polysaccharide-based hydrogel matrix [22]. In 2002, Haraguchi *et al.* reported the fabrication of novel clay incorporated HNC which possessed higher mechanical and swelling/deswelling characteristics [23]. This report is considered as an important step towards the development of HNC. Since 2008, extensive research on HNC has been carried out to develop materials that can meet the wide range of demands, including drug delivery and other biomedical applications.

However, synthesis of polysaccharide and protein-based HNCs have been carried out from 2010 onwards. Pal *et al.* developed sodium alginate-based HNC with incorporation of Ag and Au NPs for catalytic reduction of 4-nitrophenol [24]. In the last decade, extensive research has been conducted on fabrication of 'smart' HNC with various physical and mechanical properties. For instance, in 2013, Bortolin *et al.* synthesized HNC from methyl cellulose, reinforcing with MMT clay for slow-release fertilizer (SRF) application [25]. In 2017, Kato *et al.* prepared a chitosan-g-poly(acrylic acid) (PAA) biodegradable superabsorbent by graft polymerization using Ceric ammonium nitrate (CAN) as an initiator and N,N'-methylene bis-acrylamide (MBA) as a cross-linking agent for agricultural application [26]. In 2020, Sethi *et al.* synthesized a novel hydrogel based on xanthan gum and starch grafted with AA via chemical crosslinking using MBA as cross-linkers under microwave (MW) irradiation [27]. Synthesized hydrogel was employed as an oral drug delivery vehicle. In 2021, Heidarzadeh-Samani *et al.* synthesized starch-based HNC with incorporation of CNF for removal of Cd(II) ions from water [28]. Thus, it has been found that research in the field of hydrogel is developing rapidly and there are always opportunities for further research in this field and the manufacturing of materials for various kinds of applications.

1.3. Materials and methods

1.3.1. Materials

In this recent era, biobased hydrogels have received great interest because of their utilization in various practical applications across the globe. Various renewable polymers including proteins- and polysaccharides-based hydrogels are prepared using different physical and chemical cross-linking methods. Moreover, to enhance the intrinsic properties of bare hydrogel matrices and to fulfill the needs of modern applications, HNCs have been developed with incorporation of different organic or inorganic NMs [29]. Therefore, various raw materials as well as NMs and preparation methods used for fabrication of hydrogels and HNCs are summarized in this section.

1.3.1.1. Polysaccharide

Polysaccharides are carbohydrate molecules used for numerous applications that are made up of several monosaccharide units connected by glycosidic linkages. They are easily available, biodegradable, non-toxic, cost effective and biocompatible in nature. They have been widely used as precursor materials for preparation of biobased hydrogels

via physical or chemical cross-linking methods of hydrophilic monomers on their surface. Polysaccharide-based hydrogel possess excellent properties due to the presence of various functional groups on their repeating units [30]. Besides, while retaining these properties, they exhibit chemical functionality and the ability to form porous network structure. Various polysaccharides obtained from different bioresources have been utilized over the last decades for the fabrication of hydrogels, some of which are discussed in this section and their structures are presented in **Table 1.1.**

(a) Cellulose

Cellulose is a low cost, non-toxic and the most abundant polysaccharide on earth. It possesses a one-dimensional (1-D) morphology and exhibits many -OH groups on its backbone. It can be easily extracted from different sources including banana rachis, wood, sisal, etc. and can be utilized in different fields of applications such as coatings, food packaging, biomedicine, energy storage materials, etc. Moreover, it is flexible, biocompatible, biodegradable hydrophilic, and possesses suitable physical and mechanical properties. It consists of linear anhydroglucose units linked together by β-(1,4)-glycosidic linkage. It possesses excellent reinforcing capability due to the existence of glycosidic linkages and hydroxyl groups that enable the hydrogen bonds which improved the properties of polymers. Therefore, cellulose in its derivative forms and as a micro- or nano-scale reinforcing agent has been extensively explored for the production of SAH with enhanced properties to utilize in different field of applications [31,32]. In 2016, Peng *et al.* developed cellulose based HNC with incorporation of modified clay for removal of methylene blue (MB) dye from water [33]. Further, Dai *et al.* in 2018, reported carboxymethyl cellulose (CMC) based HNC reinforced with both GO and BNT clay for removal of MB dye from water [34].

(b) Starch

One of the most common polysaccharides, starch contains amylose (20-25% by weight) and amylopectin (75-80% by weight). Amylose is a linear polysaccharide made up of glucopyranose units linked by α-(1,4)-glycosidic bonds, whereas amylopectin is branched polymer and made up of α-(1,4)-glycosidic chains joined by α-(1,6)-glycosidic linkages [35]. Main sources of starch are cereals, potato, grains, corn, cassava and others [36]. Due to its inexpensive, biodegradable, non-toxic, abundant properties, it has been widely used in the preparation of biobased hydrogels via physical or chemical cross-

linking methods. Moreover, starch is often grafted with hydrophilic monomers to enhance the hydrophilicity of the prepared hydrogel. Various reports are available on the preparation of starch-based SAHs for different applications, such as Sarmah and Karak synthesized SAH using starch and AA for use as water conserving agent and nutrient carrier in agricultural applications [37]. They observed that the synthesized SAH exhibited WAC of 700 g/g and also observed slow urea release rate of the hydrogel. The presence of higher amount of biobased component makes the hydrogel biodegradable.

(c) Chitosan

Chitosan is a biopolymer obtained by partial deacetylation of the N-acetyl group of chitins, which is also the most common polysaccharide. Chitosan is composed of D-glucosamine with randomly located N-acetylglucosamine groups joined together by β-(1,4) bonds. Due to the presence of $-NH_2$ and -OH groups, it possesses hydrophilic property. Moreover, biodegradable, antibacterial, and biocompatible properties are also observed in the case of chitosan. It can be obtained from natural sources such as shrimp shells, prawns, crabs, etc. [38]. With these excellent properties, chitosan-based SAHs have been widely used for different fields of applications. For instance, Pathania *et al.* prepared chitosan and poly(AM) (PAM) based HNC with incorporation of Zn as NM using MW radiations and utilized for drug delivery applications [39]. Moreover, Butt *et al.* also developed chitosan and poly(vinyl pyrrolidone) (PVP) based hydrogels using epichlorohydrin (ECH) as the cross-linker for drug delivery system [40].

(d) Guar gum

Guar gum is another easily available biopolymer, obtained from endosperm of the *Cyamopsis psoraloides* plant. It is a biopolymer with several advantageous properties such as hydrophilicity, biodegradability, non-toxicity, and others. Guar gum composed of D-mannose and D-galactose in which the D-mannose units are linked to each other by β-(1,4) linkages, whereas the D-galactose units are linked to every second unit of mannose by α-(1,6) bonds [38]. Since guar gum has highly hydrophilic properties, it is used to develop chemically cross-linked hydrogel for different fields of applications [41]. In 2020, Sand and Vyas synthesized guar gum based SAHs using potassium persulfate (KPS) as a free radical initiator. They observed that maximum WAC of the prepared hydrogel was 80 g/g in deionized water and 22 g/g in saline solution [42].

(e) Alginate

Another linear polysaccharide, alginate can be obtained from brown seaweed. It is a non-branched, binary copolymer of β-D-mannuronic acid and α-L-guluronic acid that are connected by 1,4-glycosidic linkage [31]. It possesses many desirable characteristics such as inexpensive, abundancy, ecofriendly, biocompatibility, and others. It is also used to produce biobased hydrogels which are hydrophilic, water swelling, sustainable and ecofriendly in nature. Therefore, alginate-based hydrogels and alginate-derivatives are widely used in biomedical, agricultural, food and pharmaceutical industries [38].

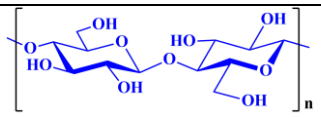
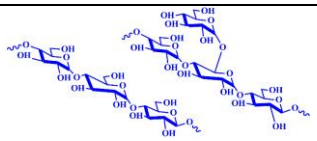
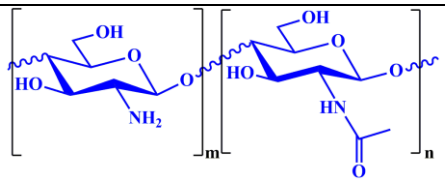
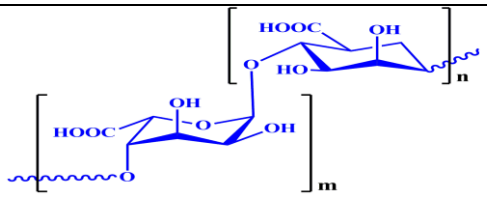
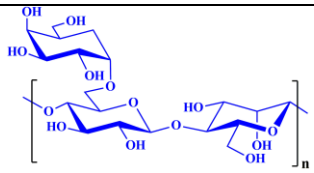
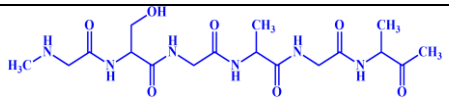
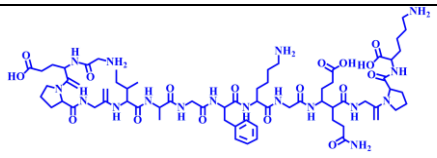
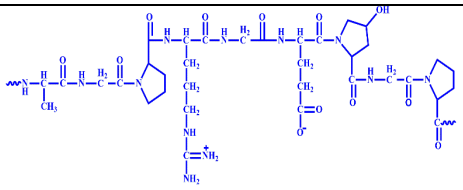
1.3.1.2. Proteins

Proteins are another important class of material for hydrogels and made up of amino acids linked together by covalent bonds. They are also utilized for fabrication of biobased hydrogels due to their biodegradable, biocompatible, injectable, and tunable nature [43]. They can also act as cross-linking agents in the fabrication of hydrogels [22]. Among various proteins, collagen, gelatin, and silk fibroin are very important and used to prepare hydrogels which are briefly discussed in this section and their structure are shown in **Table 1.1.**

(a) Collagen

Collagen is the most commonly found fibrous protein in mammals. It can be easily and inexpensively extracted from tissues due to its ubiquitous nature [44]. It self-assembles into bundles of fibers at neutral pH to form physically cross-linked hydrogels in the presence of water. Moreover, some chemical cross-linkers such as glutaraldehyde and formaldehyde are also used to produce stable hydrogel with high cross-linking density [41]. However, the use of these cross-linkers can cause possible toxic side effects that may limit their *in vivo* applications. In order to avoid toxicity, collagen concentration can be increased to increase the cross-linking density as well as by incorporating various NMs into the collagen-based hydrogel matrix [22]. Because of their biocompatible, versatile, resemblance to extracellular matrix (ECM), cost effective characteristics, collagen-based hydrogels have been extensively investigated for tissue engineering and drug delivery applications [44]. An extremely soft and multifunctional collagen-based hydrogel was prepared by Ding *et al.,* in the presence of guar gum and poly(NIPAM) (PNIPAM) using GO as the NM [45]. The resulting hydrogel possessed desirable properties such as injectability, remoldability, and processability, and they used the hydrogel to treat wounds on mouse skin.

Table 1.1. Various biobased polymers that are used in fabrication of hydrogels, their structures and applications.

Polymer	Structure	Applications	References
Cellulose		Biomedical, water remediation, agriculture	[46-48]
Starch		Agricultural products, water remediation	[49,50]
Chitosan		Agriculture, biomedical, health hygiene, water purification	[3,40,51]
Alginate		Water purification, biomedical, agricultural	[52-54]
Guar gum		Agriculture, food packaging, drug delivery	[55-57]
Silk fibroin		Wound dressing	[58,59]
Collagen		Tissue engineering, 3D cell culture	[60,61]
Gelatin		Tissue engineering, antibacterial	[61,62]

(b) Gelatin

Gelatin is a protein which is obtained from collagen by hydrolysis. Gelatin is chemically composed of 4-hydroxy proline, proline, and glycine and is also hydrophilic, biocompatible and biodegradable in nature [22]. Due to the presence of several functional groups, gelatin is easy to cross-link to form hydrogels. It dissolves easily in water in its natural form. Over the past decades, gelatin-based hydrogels have been commonly used for different application fields such as cosmetics, agricultural, biomedical, etc. [22]. Literature reports indicate that use of gelatin enhances the functionality, mechanical strength, and hydrophilicity of hydrogels [62]. Moreover, gelatin-based hydrogels have also been explored in combination with NM to fabricate biocompatible HNC.

(c) Silk fibroin

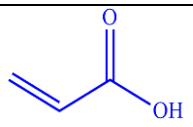
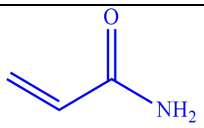
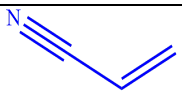
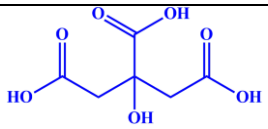
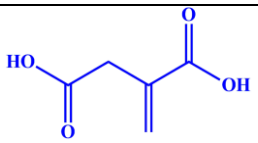
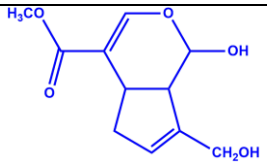
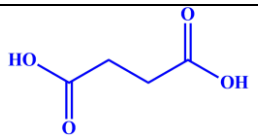
Silk fibroin is a readily available protein that is extensively used in the scaffold materials for tissue regeneration. The glands of arthropods such as spiders, mites, scorpions, flies, and silkworms are the good source of silk fibers. It is most commonly explored in the biomedical field because of its biocompatibility, elasticity, mechanical and controllable degradation properties [63]. Due to these properties, silk fibroin-based hydrogels have fascinated considerable attention from researchers around the world. Further, in recent years, hydrogels based on silk fibroin possess properties like self-healing, external stimuli-responsive, injectable, adhesive and 3D printing, leading to their application in the fields of biosensing, cosmetics, textiles, and food [59]. Moreover, to fabricate silk fibroin-based hydrogels with improved properties, the fabrication of corresponding HNC has fascinated the interest of researchers from all over the world.

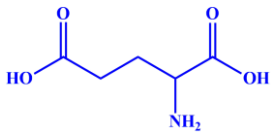
1.3.1.3. Monomers

In recent decades, most of the hydrogels have been synthesized using various vinyl monomers including AM, MAM, AN, vinyl acetate (VAc), methacrylic acid (MAA), vinyl sulphonic acid (VSA), HEMA, N-vinyl pyrrolidone (NVP), AA, etc. which are mostly used chemicals in industrial polymerization. However, these non-biodegradable synthetic monomers, which are obtained from nonrenewable resources, have limited their widespread application fields because of their poor/non biodegradability and high toxicity [64]. Therefore, polysaccharides and proteins are used as raw materials to develop biobased hydrogels to avoid utilization of petroleum-based monomers. However, to enhance water swelling capacity of hydrogels, hydrophilic groups are

introduced via grafting of vinyl monomers (e.g., AA, AM, AN etc.) in biopolymers. Besides hydrophilicity, hydrogels also exhibit external stimuli responsive, adsorption behavior, etc. [65]. Moreover, biobased monomers such as IA, citric acid (CA), Tulipalin A, succinic acid (SA), and glutamic acid (GA), etc. are also used as monomers for fabrication of hydrogels. Structures of some bio- and synthetic-based monomers used to prepare hydrogels along with their applications as well as chemical structures are presented in **Table 1.2.**

Table 1.2. Various monomers that are used for fabrication of hydrogel, their structures, and applications.

Monomers	Structures	Applications	References
AA		Agriculture, wastewater treatment, pigment printing, drug delivery	[49,66,67]
AM		Controlled delivery of bioactive agent, water remediation	[60,68,69]
AN		Wastewater treatment, sensor	[70,71]
CA		Drug delivery, wound dressing	[72,73]
IA		Drug delivery, wastewater treatment	[74,75]
Genipine		Drug delivery, wound dressing	[76,77]
SA		3D bioprinting, drug delivery	[78,79]

GA		Wound healing, tissue engineering	[80,81]

1.3.1.3.1. Biobased monomers

In the last few decades, numerous biobased monomers have been used to fabricate biodegradable, non-toxic, and biocompatible hydrogels. They are obtained from various bio-resources and utilized for different potential applications. Some biobased monomers are briefly described below.

CA is an ecofriendly, multifunctional, non-toxic, biodegradable, and biobased monomer obtained from less expensive materials and used in food, chemical, and biomaterial production industries [82]. It possesses three -COOH and one -OH groups which are responsible for its hydrophilic property and also provide cross-linking sites during the formation of hydrogel. CA is used as a monomer as well as a `cross-linker for wide variety of applications.

IA is also used as a biobased monomer, obtained using distillation of CA and fermentation of sugars [83]. In 1836, Baup discovered the synthesis of IA from distillation of CA. It has been utilized as a monomer to develop ecofriendly and biocompatible hydrogel due to its structural analogy to AA and MAA. It is composed of vinyl group and two -COOH groups. From the literature report, it is observed that IA undergoes self-polymerization or copolymerization with other vinyl monomers [84]. It has enormous potential in wide applications such as agriculture, pharmaceutical, biomedical, etc. due to its biocompatibility, antimicrobial, wound healing, biodegradability, and chemical reactivity [82,85]. Various studies have been reported on the fabrication of IA containing hydrogels. In 2017, Sood *et al*. developed a hydrogel by grafting IA and lactic acid (LA) on the surface of CMC under MW irradiation to investigate controlled drug release profiles and antibacterial activity against *Staphylococcus aureus* (SA) and *Escherichia coli* (EC) bacterial strains [74]. They observed that antibacterial activity of the prepared hydrogel increased with the increase in IA concentration. Moreover, controlled release profile for amoxicillin was observed in acidic conditions.

Nowadays, SA has been considered as a promising biobased monomer and obtained from fermentation of carbohydrates such as sucrose, glucose, fructose, etc. [82]. It is a

dicarboxylic acid as well as it possesses biocompatible, non-toxic, and biodegradable nature. It possesses great potential in the fields of food, cosmetics, medicine, agriculture, etc.

GA is also a biobased monomer obtained from microbial fermentation. The German chemist Karl Heinrich Ritthausen discovered and identified GA in 1866. It has been explored in the food, agriculture, pharmaceutical, water treatment and other industries owing to its biocompatible, non-toxic, and biodegradable nature [82]. It has been widely used in fabrication of hydrogel through cross-linking with natural or synthetic polymers.

1.3.1.3.2. Synthetic based monomers

Synthetic monomers have extensively attracted for preparation of hydrogels because they possess excellent swelling and adsorption capacity, reusability, high processability, extended service life. However, they have biodegradable issues and possess toxic effects in human beings and animals, so their use for hydrogel fabrication is avoided as much as possible. Therefore, to reduce the use of toxic monomers, biobased hydrogels are prepared by grafting certain amounts of synthetic monomers onto polysaccharide backbone to obtain enhanced properties. Some commonly used petroleum-derived monomers are discussed below.

AA is one of the most commonly used monomers to prepare hydrogels as it can easily react with free radicals and electrophilic reagents [86]. It is conventionally obtained from petroleum-based sources. Moreover, it is also generated by partial oxidation of propene. The presence of AA can enhance water swelling capacity, pH sensitivity and ionic strength of hydrogels. AA-based hydrogels exhibit high swelling capacity at basic pH due to electrostatic repulsion between carboxylate ($-COO^-$) groups generated by deprotonation of the -COOH group. Moreover, AA together with some other monomers are also used to prepare different hydrogels [87]. Further, they have been extensively explored in numerous fields due to their excellent properties.

AM is another synthetic monomer which is most commonly used for preparation of hydrogels, and it has also attracted significant attention in numerous fields of applications. It is a neutral and hydrophilic monomer as well as it possesses favorable chemical and physical properties for utilization in different applications. They are also responsive to external environmental conditions [87]. Typically, AM-based hydrogels are prepared via free radical polymerization method using different cross-linkers.

Besides AA and AM, various other petroleum-based vinyl monomers such as MAM, AN, VAc, MAA, VSA, HEMA, NVP, etc. have also been used to prepare hydrogels.

1.3.1.4. Cross-linkers

In 1998, Kawakami and Kato developed bis-pyridine molecule as a cross-linker for the first time [88]. Since then, numerous cross-linking molecules have been developed for fabrication of different polymeric materials. Various cross-linkers such as MBA, ethylene glycol dimethacrylate (EGDMA), CA, genipine, ECH, ethylene glycol diglycidyl ether (EGDGE) are used as integral parts in the formation of the 3D network structure of hydrogels [67,89]. In **Figure 1.1**, structures of various cross-linkers are presented. Due to the presence of cross-linking agents, hydrogels can swell water many times to its dry weight without dissolving into the medium. The amount of cross-linker used also affects the characteristic properties of the hydrogel. When cross-linker concentration increases, the cross-linking density of the hydrogel increases, leading to higher hydrogel strength, whereas lower swelling capacity is observed for this [90]. In 2017, Xiao *et al.* prepared SAH by grafting AM on starch and using MBA as the cross-linker for SRF applications [91]. They observed that as the amount of MBA increased, the water swelling capacity decreased significantly. In another work, Thombare *et al.* synthesized guar gum and AA-based hydrogel using EGDMA as the cross-linker [55]. They also observed that beyond a certain amount of cross-linker, swelling capacity decreased as the EGDMA content increases.

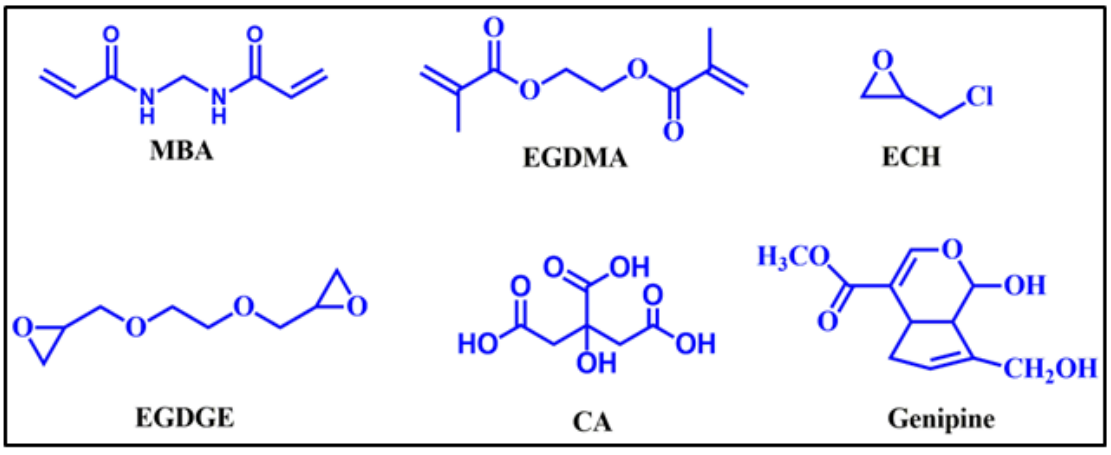


Figure 1.1. Structures of various cross-linkers.

1.3.1.5. Nanomaterials (NMs)

NMs are organic or inorganic materials having at least one dimension in nanoscale range i.e., from 1 to 100 nm. Based on their dimension they are categorized into three classes, i.e., zero dimensional (0-D), one dimensional (1-D) and two dimensional (2-D) NMs. All dimensions of 0-D NMs are in nanoscale range. However, one or two external dimensions only are within the nanoscale range for 1-D and 2-D NMs, respectively. For the last two decades, NMs have been extensively explored in every possible field of applications as reinforcing agent due to their high surface area and physicochemical properties [92]. Moreover, incorporation of these NMs enhances the properties of conventional hydrogels without affecting their intrinsic properties. There are many kinds of NMs with different shapes such as rods, spheres, wires, tubes, etc. All kinds of NMs have the potential to be incorporated into the hydrogel matrix to obtain HNCs. Moreover, to improve the affinity of NMs, some functional groups on the surface of NMs are introduced by modification techniques. Different types of NMs and their utility in fabricating hydrogels are briefly discussed below.

1.3.1.5.1. Cellulosic NMs

In the last decades, cellulosic NMs such as CNFs, CNWs, cellulose nanocrystals (CNCs) have been widely explored because of their inexpensive, biocompatible, and modifiable nature. Their chemical structure consists of anhydroglucose units which are connected by β-(1,4)-glycosidic linkages. Cellulosic NMs can be modified through reactions including etherification, esterification, oxidation, etc., due to the presence of reactive -OH groups on their surface, enabling them to be uniformly distributed within the polymer matrix, leading to improvement in their properties [93]. They have been used for wide applications such as hygiene products, medical, food, pharmaceutical, cosmetics, etc. [94]. Different NMs isolated from cellulose are briefly described below.

(a) CNFs

In 1983, Herrick *et al.* performed pioneering work in the production of CNFs from cellulosic wood pulp utilizing a mechanical homogenizer [95]. They are 1-D carbon-based NMs which can be easily extracted from bioresources such as wood, plants, banana rachis, algae, bacteria, etc. Nowadays, waste materials such as wastepaper (WP) [96], coconut shells [97], corn stalks [98], etc. are also used to isolate CNFs instead of using fresh plant sources. They have received significant interest for different fields of applications due to their renewable, optical, biodegradable, large specific surface areas.

Several approaches i.e., enzymatic hydrolysis, acid hydrolysis and mechanical treatments (such as high-pressure homogenizers, microfluidizers, and steam explosion) are used to produce CNFs [99,100]. Recently, modification of CNFs has been carried out via etherification or esterification reaction to improve dispersibility as well as increase the applicability of CNF [101]. Nowadays, CNF and its derivatives are widely used as NMs in fabrication of HNCs to enhance the properties of bare hydrogel matrix. Zhou *et al.* synthesized CMC, AA, and AM-based superabsorbent using modified-CNF (mCNF) as reinforcing agent [102]. They observed a significant increase in swelling capacity from 245.8 to 458.7 g/g in distilled water due to the addition of mCNF. Further, they observed that the addition of mCNF also improved salt resistance property of the hydrogel. In 2021, Liu *et al.* developed sodium alginate and PVA-based hydrogel in the presence of CNF to use as a fertilizer (NPK) release system in agricultural applications [54]. The results suggested that due to the incorporation of CNF, the hydrogel showed SRF property and only released 24.82%, 36.21%, and 50.17% of N, P and K nutrient elements, respectively within 30 days. Further, the hydrogel exhibited higher water retention capacity in both water and mixed soil.

(b) CNCs

CNC is an important class of 1-D cellulosic NMs which is obtained by strong acid hydrolysis of cellulosic raw materials by using sulfuric or hydrochloric acid. It is obtained from several bioresources including cotton, rice husk, wood, algae, sugar beet, etc. [103]. It contains higher crystallinity compared to CNFs and possesses wire-like morphology. The diameter of CNCs usually vary from 5 to 70 nm and their length typically ranges from 100 to 250 nm. However, dimension of CNCs often depends on the source of cellulose, agitation, hydrolysis time, etc. [104]. According to literature reports, CNCs are partially dispersible in water due to the presence of negatively charged -SO_3H groups that can be introduced during acid hydrolysis. Usually, dispersibility of CNC is improved by surface modification using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [105]. Over the past decades, CNC has emerged as a promising NM for fabrication of HNCs due to its biocompatible, biodegradable, and ecofriendly nature. Moreover, their hydrophilicity, cytocompatibility and non-toxic nature make them potential materials for biomedical, water purification and biosensing applications. In 2020, Olad *et al.* prepared semi-interpenetrating hydrogel composite based on starch and PVA via free radical polymerization method [106]. CNC was incorporated into the hydrogel as NM to

improve the properties of the bare hydrogel matrix. From the swelling results, it was noticed that addition of CNC increased water swelling capacity from 772 to 921 g/g. Additionally, the hydrogel composite showed high saltwater absorption under load and pH-sensitive reversible swelling behaviour which make it a potential candidate for horticultural and agricultural applications.

(c) CNWs

Recently, CNWs have been extensively used as a reinforcing agent for the preparation of HNCs due to its high surface-to-volume ratio and Young's modulus [107]. They are highly crystalline in nature, obtained by acid hydrolysis of cellulose and possess a rod-like shape with length as much as 500 nm and width varying from 3 to 15 nm [93]. CNWs exhibits properties including inexpensive, renewability, high biocompatibility, easy modification, etc. Recently, CNWs incorporated hydrogels are prepared to obtain enhanced water uptake capacity and mechanical properties compared to the bare hydrogels. For instance, Muniz *et al.* developed starch and AA-based HNC using CNWs as NM and investigated the swelling property of the HNC [108]. They observed increase in swelling capacity with the increase of CNWs content. Moreover, Alvarez *et al.* also prepared PVA-based HNC with the incorporation of CNWs for wound dressings [109]. The results indicated that due to the incorporation of CNWs, HNC possesses improved mechanical and thermal properties as well as suitable water vapor transmission rate, making the hydrogel a potential material for biomedical applications.

1.3.1.5.2. Metal/metal oxide nanoparticles (NPs)

Since the last century, research on the metallic NPs has been extensively carried out in different fields of applications due to their extremely small size as well as large surface area [110]. Moreover, they possess excellent properties such as antibacterial as well as photocatalytic activity, optical, electronic, physical, and chemical stability, etc. [111]. According to the literature, various metal or metal oxide NPs such as Fe_3O_4, Ag, MgO, ZnO, CuO, TiO_2, etc. are used to enhance the conventional properties of bare hydrogel matrix. Among them, ZnO, CuO and Ag NPs have attracted more attention towards biomedical, food, cosmetics, and hygienic products, due to their excellent UV barrier and antibacterial properties. Various methods are used for preparation of metal or metal oxide NPs such as homogeneous precipitation, sol-gel processing, thermal evaporation, MW method and mechanical milling [112]. However, these methods are costly,

laborious, and environmentally hazardous. Therefore, a green chemistry approach has emerged for the synthesis of NPs using numerous leaf extracts including *Thuja Orientalis* leaf extracts [113], *Eucalyptus globulus* Labill leaf extracts [114], etc. In this regard, the synthesis of various NPs using green synthesis approach have been reported for different application fields, such as, Pandian *et al.* synthesized Ag NPs using *Aloe vera* plant extract and studied their antimicrobial activity [51]. Moreover, using *Carica papaya* leaf extract, ZnO NPs were prepared by Chauhan *et al.* in 2020 [115]. They studied antifungal property and effect of ZnO NPs on germination of chickpeas.

1.3.1.5.3. Nanoclay

Nanoclays are widely available inorganic reinforcing agents. They are extensively used as a NM in polymer matrices to enhance their intrinsic properties (such as water swelling capacity, ion exchange capacity, adsorption capacity, etc.). They are 2-D NMs having only 1-D in nano scale range [116]. Kaolinite, illite and MMT are the most commonly used clays due to their cost effectiveness, high surface-to-volume ratio, easy availability, cation exchange capacity, etc. [117]. Recently, the development of clay incorporated HNCs have attracted special attention in numerous fields, including biomedical, wastewater treatment, agriculture, etc. For instance, Rashidzadeh *et al.* prepared a HNC by grafting AA and AM on sodium alginate in the presence of clinoptilolite via free radical polymerization method to study the release rate of fertilizer from the hydrogel [118]. It was observed that the HNC released less than 57% of loaded fertilizer within 30 days and showed maximum WAC of 34 g/g. The water retention ratio of soil with NPK-loaded HNC was 85 and 69% on 15^{th} and 30^{th} days, respectively which are higher than those of untreated soil. In 2017, Liu *et al.* prepared an eco-friendly and non-toxic composite hydrogel from CMC with incorporation of MMT clay as the reinforcing material in order to remove cationic MB dye from water [119].

1.3.1.5.4. Graphene oxide (GO)

In 2004, graphene was discovered by Andre Geim and Konstantin Novoselov [120]. Since then, graphene has attracted considerable attention from different fields of researchers. GO is one of the prominent materials that plays an crucial role in the development of graphene and its derivatives [121]. GO nanosheets are 2-D carbon-based NM and composed of sp^2-/sp^3-hybridized carbon atoms. They contain huge number of -OH, C=O, epoxy groups on their surface and are easy to disperse uniformly in water as

well as other organic solvents. GOs are prepared by using different approaches such as Staudenmaier, Brodie, Tour, and Hummer's methods [122]. Due to lower production cost and excellent physical properties, GOs has been explored as promising reinforcing agent for preparation of HNCs [123].

1.3.1.6. Nanohybrid

Recently, preparation of metal oxide nanohybrids has drawn a considerable attention from the material science researchers due to their versatile properties [124]. Many literatures have been reported on fabrication of nanohybrid for numerous applications including wastewater treatment, biomedical, etc. [125,126]. Nanohybrid is a combination of two or more organic, inorganic components, or an intimate mixture of organic and inorganic elements that synergistically improve the functionality of the resulting material. Metal or metal oxide NPs often undergo agglomeration during synthesis due to their high specific surface area as well as high surface energy. To overcome this issue, NPs have been synthesized using cellulosic NMs as the supporting material to improve the dispersion of NPs. Since cellulosic NMs possess numerous -OH groups which can also be easily functionalized, leading to the stabilization of metal or metal oxide NPs via electrostatic interactions. Thereby, development of nanohybrid is an effective way to mitigate NP aggregation [127].

1.3.2. Methods

1.3.2.1. Methods for preparation of hydrogel

The preparative methods of hydrogels include physical and chemical cross-linking strategy. Physical cross-linking method includes preparation of hydrogel without any chemical cross-linker and thus, these methods are comparatively safer than the chemical cross-linking method. Moreover, physical cross-linking methods include formation of hydrogen bond, electrostatic interactions, ion exchange, π-π interactions, etc. [128]. However, mechanical weakness, structural imperfections, reversible nature, etc. are some serious drawbacks, due to which preparation of hydrogels using chemical cross-linkers are gaining much more attention [129]. Strong covalent interactions are present within the hydrogel network in the case of chemically cross-linked hydrogels, making them stable in nature [128].

Chemical cross-linking methods can be divided into various sub-categories including direct cross-linking by using small molecules, free radical polymerization and grafting.

Various monofunctional and bifunctional molecules such as formaldehyde, glutaraldehyde, ECH, genipin, EGDGE, diethyl squarate, etc. are extensively used for direct chemical cross-linking methods [130].

The free radical mechanism of hydrogel preparation involves a three-step process: (a) initiation, (b) propagation and (c) termination of polymer chains [87]. The existence of initiators such as unimolecular initiator, light, redox initiator, heat, MW, etc. activates the chains which further react with the double bond of vinyl monomers to propagate the active chains. The presence of cross-linkers forms a network with the polymeric chains. Further, the chains are terminated by combination, or disproportionation, or other chain transfer processes. The initiator used in this process are KPS, CAN, ferrous ammonium sulfate, ammonium persulfate (APS), azobisisobutyronitrile (AIBN), and benzoyl peroxide (BPO), etc., while MBA, EGDMA, etc. are the most commonly used cross-linkers which are generally used to cross-linked various vinyl monomers such as AA, AM, HEMA, vinyl chloride, etc. [130].

In grafting methods, the polymerization of monomers occurs on the backbone of polymers, usually polysaccharides. To activate the polymer chain, various types of initiators are used followed by grafting of the polymerizable monomer in the presence of cross-linking agent. Various hydrophilic monomers such as AA, AM, etc. are widely grafted on polysaccharides. Depending on the source of activation, grafting can be divided into radiation grafting and chemical grafting. Chemical grafting methods involve the utilization of chemical initiators such as APS, BPO, etc. while radiation grafting methods include UV-radiation, MW radiation, gamma-radiation, etc. [131].

Besides free radical and grafting method, chemically cross-linked hydrogels can also be synthesized by direct cross-linking method. In this method, cross-linking of functional groups of natural or synthetic polymer chains is carried out with monomers via condensation reaction [3]. Several functional groups such as -NH_2, -OH, -COOH are responsible for cross-linking of the hydrogels in which multifunctional polymer is gradually added along with the monomers. Various monomers like TEMED, ECH, CA, etc. are used to form hydrogel in this method [132].

1.3.2.2. Methods for preparation of NMs

Generally, there are two approaches used to prepare NMs, which are top-down approach and bottom-up approach. In the top-down approach, a solid bulk material is broken down into small parts using numerous methods such as ball milling, mechanochemical,

electrochemical, etc. However, the bottom-up approach includes formation of nano sized materials from the atomic or molecular level using numerous methods including pyrolysis, condensation, etc. [133]. The methods used for preparation of NMs are further divided into three types which are biological, physical, and chemical methods. Various chemical methods such as co-precipitation, hydrothermal, MW, etc. used to fabricate NMs are briefly described in this section [134].

The co-precipitation method is one of the most frequently used techniques for synthesis of NPs. This method also has the advantage of low production costs as well as easy preparation techniques. The method involves mixing two or more water soluble metal salts, undergoes precipitate reaction and subsequently forming NPs [135].

Another commonly used method to prepare NMs is the hydrothermal approach which includes aqueous or non-aqueous solvents. The method involves dissolving the reactants in an appropriate solvent, mixing the liquid phase, and subsequently, subjecting the resulting mixture to high temperature and pressure [136].

Moreover, the MW method is also extensively used due to the advantage of consuming less time for formation of NMs. In this method, electromagnetic energy is converted into thermal energy that heats the material to generate NMs [135].

Further, cellulose has also been explored to develop various micro- or nano-reinforcing agents with different shapes and degree of crystallinities. They can be isolated from cellulosic raw materials using a top-down approach by applying different chemical treatments including acid, alkali, bleaching, etc. [137].

1.3.2.3. Methods for preparation of HNCs

In spite of the remarkable developments observed with bare hydrogels, they are still far away from achieving the growing demand for high-performance polymers. Therefore, the idea of developing HNCs has emerged. The incorporation of NMs introduces some extraordinary properties into the bare hydrogel matrix. Moreover, performances of the HNCs mainly depend on the composition of the hydrogel matrix, type and amount of the NMs, and also the size as well as the distribution of the NMs within the hydrogel network [29]. Generally, three different techniques are used for fabrication of HNCs; the first one is the simplest one and includes the polymerization of monomers or prepolymers in presence of NM. In this technique, use of cross-linker is necessary and the application of mechanical agitation during the polymerization process provides uniform distribution of NM in the reaction mixture [91,138]. In the second technique,

separately prepared NMs are entrapped into pre-formed hydrogel matrix based on the interaction force generated between them [139,140]. In the third technique, previously functionalized NMs are allowed to interact with biopolymers to prepare corresponding HNC. In this method, NMs are used as cross-linking agents. Therefore, it does not require the use of additional cross-linker, which makes the prepared HNC free from the toxicity of cross-linking agents [141,142].

1.4. Characterization and analysis

The hydrogels, NMs along with their corresponding HNCs are characterized using various analytical, microscopic, and spectroscopic techniques to investigate their physicochemical nature. A brief description of all these techniques is given in this section, as follows.

1.4.1. Spectroscopic techniques

1.4.1.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is a commonly used basic analytical technique which is utilized to recognize the presence of different functional groups in the prepared hydrogels, reinforcing agents and HNCs. In this technique, key functional groups of molecules vibrate due to the absorption of IR radiation within the wavelength of 4000-400 cm^{-1} [143]. The characteristic peaks for the prepared hydrogels were observed at around 3400, 2900, 1700 and 1060 cm^{-1} corresponding to -OH, aliphatic CH_2, C=O and C-O-C groups, respectively supporting the successful preparation of the hydrogels [144]. Moreover, this technique is also useful in understanding the formation and modification of the prepared cellulosic reinforcing agents. This technique is also used to evaluate the changes in chemical structure of the prepared hydrogel during biodegradation [66].

1.4.1.2. Ultraviolet-visible (UV-vis) spectroscopy

UV-vis spectroscopy is another most prominent spectroscopic metho used for the characterization of metal or metal oxide NPs. Generally, the typical surface plasmon resonance (SPR) peaks of NPs arise at wavelength of 200-800 nm due to the interaction of UV radiation with the surface electrons of NPs. For instance, the SPR peak of zinc oxide NPs was observed at around 360 nm [145]. Moreover, molecules having unsaturated and conjugated moieties are also characterized using this technique due to their electronic transition such as $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and charge transfer upon exposure of UV radiation [146]. Additionally, this technique can also be utilized to study dye adsorption

capacity [146], slow release of urea as well as NPK fertilizer [147], and controlled drug release [148].

1.4.1.3. X-ray photoelectron spectroscopy (XPS)

XPS is a surface sensitive, non-destructive technique utilized to determine the elemental composition on the surface of the material. Moreover, oxidation state and electronic structure of the material can also be elucidated using this technique. In this method, a sample is irradiated with a monochromatic photon, which causes the emission of photoelectrons from different energy levels of all elements in the material to be quantified, and the results are then obtained [149]. Further, presence of different metals in the NMs and within the network structure of the hydrogel can also be detected from this technique. Thus, elemental composition and chemical bonds present in samples can be evaluated using this technique combined with FTIR spectroscopy [150].

1.4.2. Diffraction technique

1.4.2.1. X-ray diffraction (XRD)

XRD is most commonly used non-destructive analytical technique which is utilized to evaluate the degree of crystallinity and phase purity of reinforcing agents as well as hydrogels [143]. The crystallinity index (C.I.) of reinforcing agents like CNFs is estimated from XRD pattern using the following equation (**Eq 1.1**) [47].

$$\text{C.I. (\%)} = \frac{I_{200} - I_{AM}}{I_{200}} \times 100 \qquad \textbf{(Eq. 1.1)}$$

Where I_{200} indicates the maximum intensity of the peak corresponding to (200) plane and I_{AM} indicate the minimum intensity between the two peaks belonging to (110) and (200) planes.

1.4.3. Microscopic techniques

1.4.3.1. Scanning electron microscopy (SEM)

SEM is a microscopic technique utilized to investigate the surface morphology and topography of reinforcing agents and hydrogels. To obtain the image, the surface of the sample is scanned with high energy focused electron beams that are scattered back after hitting the surface. The resulted electron beams due to the elastic and inelastic interactions between the electron beam and sample surface are known as back scattered electrons and secondary electrons detected by solid state detector and Everhart-Thornley

detector, respectively. From this technique, it is also possible to study the shape, size as well as dispersion of the reinforcing agents within the surface of the hydrogel matrix [151,152]. Further, surface of the biodegraded samples can also be studied using this technique. Moreover, EDX spectrophotometer attached to SEM also provides the atomic weight percentage of the elemental compositions of reinforcing agents and hydrogels [153].

1.4.3.2. Field emission scanning electron microscopy (FESEM)

FESEM is another microscopic technique used to study the surface morphology of a sample with higher resolution and the resulting images are of better quality compared to SEM. Differences are observed due to the use of different electron producing systems. In FESEM, a field emission gun is used for emission of electron beams. However, a heated tungsten filament is used as an electron emission source in the case of SEM. This technique is better to investigate the surface morphology of the reinforcing agents [154].

1.4.3.3. Transmission electron microscopy (TEM)

TEM is considered as an important microscopic technique for the characterization of NMs. Using this technique, the size, shape, and uniformity of the particles can be determined. In this technique, a beam of high energy electrons interacts with an ultrathin part of the specimen and some parts of the beam transmitted through the specimen, while remaining parts of the beam are scattered. The transmitted beam provides resultant image of the internal structure based on the elemental composition and density of the sample [155].

1.4.4. Other technique

1.4.4.1. Thermogravimetric analysis (TGA)

TGA is employed to study the thermal stability of the NMs and hydrogels by comparing their weight loss (%). Moreover, the presence of reinforcing agents and inorganic elements in the hydrogel matrix can also be determined from this technique. Further, the first derivative thermogram (DTG) of the TGA provides information regarding on-set temperature (T_{on}), maximum degradation temperature (T_{max}), and degradation pattern of the samples [156].

1.4.4.2. Dynamic light scattering (DLS) and Zeta potential (ZP)

DLS technique is used to characterize and determine the size and size distribution of NPs. However, due to the solvation effect, the size of the NPs obtained by this technique is usually larger than the XRD and TEM analysis. Moreover, ZP is also an important tool to investigate the colloidal behavior of NPs. According to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, higher charge density on the surface of particles leads to stronger electrostatic repulsion between the particles, leading to higher stability of NPs [157].

1.5. Testing methods

1.5.1. Water swelling

The equilibrium WAC of the synthesized hydrogels is measured by the gravimetric method [158]. The method involves immersion of a calculated amount of dry hydrogel in excess water. Thereafter, the water swollen hydrogel was removed from the swelling medium and water remains on the surface is wiped off using a steel sieve or tissue paper. After measuring the weight of the swollen hydrogel, it is kept in the same medium. This process is repeated until an equilibrium WAC is achieved [159].

1.5.2. Fertilizer loading and its release

Over the past decades, hydrogels have been widely used as SRF system for sustain release of fertilizer. There are two approaches of fertilizer loading i.e., *in-situ* loading and post loading method. In the post loading approach, the preformed hydrogel is immersed in the desired fertilizer solution, where the nutrients penetrate into the hydrogel network structure through absorption, while the *in-situ* loading approach includes loading of nutrients during hydrogel preparation. The *in-situ* approach is considered preferable to the post-loading one due to its higher loading efficiency [159].
Further, the fertilizer release test is carried out by immersing the fertilizer encapsulated hydrogel in a certain volume of the desired medium. After immersing for a predetermined time period, a specific volume of the supernatant liquid is taken out and the amount of nutrient released by the hydrogel into the medium is determined using different analytical techniques [160].

1.5.3. Seed germination

Since the plant growth and crop yield are usually affected by drought conditions in arid and semi-arid areas, SAHs with high water swelling capacity and slow-release properties

are used in agronomy [161]. In this regard, to investigate the effects of prepared hydrogels on seed germination rate, root length (RL) and shoot length (SL) of the plants compared to bare soil medium, this experiment is carried out [162]. For germination rate, seeds are considered as germinated, when 1-2 mm of radicles first appeared, and RL and SL are measured with a ruler after a predetermined period.

1.5.4. Adsorption

This is the most frequently utilized method to measure the removal capacity of prepared hydrogels for heavy metal ions and organic dyes from contaminated water. Hydrogels are highly recommended for this purpose because of their porous 3D network structure as well as their ability to absorb salt solution [163]. From this test, the effect of different parameters, including solution pH, temperature, adsorption time, etc. on removal capacity of the hydrogel, can be studied. Moreover, this method is highly effective, efficient, economical and does not cause secondary pollution [164]. The efficiency of this test depends mainly on the type of hydrogel used, the nature of the contaminants, and the interactions that take place between the hydrogel and the contaminants [48].

1.5.5. Biodegradation

Biodegradability is considered as one of the most essential properties of hydrogel for agricultural application, because long-term retention of polymeric materials in soil can cause severe environmental pollution [160]. In this regard, the soil burial method is usually applied to investigate the biodegradation of hydrogels. This is a simple method that resembles actual field conditions for waste treatment [9]. This method involves burying samples under specified soil for a certain period of time. After a predetermined time, a sample is taken out and biodegradability is determined in terms of percentage weight loss along with FTIR and SEM image analyses [160].

1.5.6. Hemocompatibility

Hemocompatibility test is carried out as a preliminary method for the safe uses of newly developing materials. This test allows to observe the hemocompatibility of biomaterial by investigating the sample’s ability to damage red blood cells (RBCs). If RBCs lysis upon contact with the material, the material being tested is considered as not safe or biocompatible or vice versa. The percentage of hemolysis is quantified by determining optical density (OD) of supernatant at 540 nm [165].

1.5.7. Antibacterial test

The agar well diffusion method is applied to observe the antibacterial activity of the prepared samples against gram-positive and gram-negative bacterial strains. For this, bacterial strains are cultured in Luria Broth (LB) overnight. Then, LB plates are prepared by evenly spreading each bacterial strain to carry out the test. Thereafter, samples with desired concentration are placed onto the LB plates and kept in an incubator for overnight. Finally, antibacterial activity of the samples is studied from their respective diameter zone of inhibition [166].

1.6. Properties

Biobased hydrogels have attracted significant interest due to their excellent properties, thus, they are widely used in various application fields. Moreover, their properties can be easily tuned according to a specific application by changing the monomer ratio, cross-linking density, and polymer-reinforcing agent interactions, etc. Some common properties of hydrogels are outlined in this section.

1.6.1. Water swelling

As hydrogels are hydrophilic polymers, swelling is the most important property of them. Swelling allows penetration of large volume of water molecules into the 3D network of the hydrogel without disintegrating their structures. Actually, swelling is the most intrinsic property which defines the existence of hydrogels. Besides water, they can also absorb biological or saline solution into their network structure and can retain for long period of time. Moreover, their swelling capacity depends on several parameters such as amount of cross-linker, initiator, monomer, neutralization degree, pH of the solution, reaction temperature, etc. [3]. When cross-linking density increases, the strength of the SAH increases but the swelling capacity decreases. Therefore, the balance between these two properties determines the final WAC of the SAH. Further, WAC also varies depending on the monomer concentration. As the monomer concentration increases, cross-linking and chain coiling also increases, leading to a decrease in water swelling capacity. Moreover, degree of neutralization of SAHs is another important factor in achieving maximum WAC [57].

1.6.2. Stimuli responsive swelling capacity

Swelling capacity of ionic hydrogels is found to be sensitive towards the pH and ionic strength of the swelling medium. As the ionic strength increases, osmotic pressure generated within the hydrogel network structure reduces, leading to a decrease in the

swelling capacity of hydrogel. Marandi *et al*. observed the effect of cations with different radii and charges on the swelling capacity and found that as the charge on cations increased the water absorbency decreased due to increased cross-linking density [68]. Moreover, cations with a smaller radius can bind strongly to the anionic site of the polymer chain, resulting in a lower WAC.

Moreover, the pH of the swelling medium also affects the swelling capacity of ionic SAHs. Reddy *et al*. observed an increase in the equilibrium swelling capacity of pH sensitive guar gum-based hydrogel when the pH of the swelling medium increased from 2 to 8 [167]. They observed that as the pH of the solution increased, deprotonation of the -COOH groups produced COO^- groups that increased the interelectronic repulsion within the network structure, leading to an enhancement of the WAC.

Further, in the case of HNCs, addition of NMs affects the external responsive behavior of bare hydrogel matrix. Besides temperature, pH and ionic strength, HNCs showed light, magnetic and electric field responsive behaviors. Usually, the nature of NMs, hydrogel matrix or combination of NM and hydrogel matrix are responsible for fabrication of those stimuli responsive HNCs [168,169].

1.6.3. Water absorption under load (AUL)

The water AUL is a measurement of the WAC of hydrogel under a certain load. It plays an important role in measuring strength of hydrogels for practical applications such as agriculture, hygiene products, etc. In contrast to free water swelling, AUL increases with increasing cross-linking density, indicating that AUL is directly proportional to the mechanical strength of hydrogels [38]. Moreover, the particle size of SAH also affects the AUL value. Small particles with high surface-to-volume ratio possess higher WAC in free water swelling test, however, when the sample is under certain load, higher AUL is observed for particles with greater size compared to small size particles [57].

1.6.4. Slow-release fertilizer (SRF)

Biobased hydrogels have been extensively studied in agriculture due to their SRF property. The SRF is one of the most noteworthy features of SRF system, which enhances nutrient absorption while minimizing nutrient loss [170]. Application of hydrogel as SRF system could be used as a promising strategy to reduce fertilizer loss, improve efficiency of use, and combat leaching pollution [171]. The slow-release property of hydrogels is mainly affected by cross-linking density, polymer type, pH, and

ionic strength of the solution. To investigate the SRF property, Jamnongkan *et al.* fabricated a hydrogel from chitosan and PVA using glutaraldehyde as a cross-linker [147]. They studied the water swelling, water retention and fertilizer release behaviors of the prepared hydrogel. After 30 days of incubation, it was observed that about 75% of loaded phosphorous fertilizer was released. Further, the water swelling and water retention of soil containing the hydrogel were found to be 232 and 20%, respectively, during 30 days of incubation, indicating the potential of the hydrogel to be use as a SRF system.

1.6.5. Dye or metal ion removal capacity

Hydrogels are emerging as promising adsorbents for removal of contaminants including organic dyes, pesticides, organic micro pollutants, heavy metal ions, etc. from wastewater. The porous 3D structure and polar functional groups of hydrogels promote excellent adsorption capacity for removing pollutants from contaminated water [173]. Particularly, the porous structure of hydrogel provides large specific surface areas for adsorption of metal ions which are capable of binding with the polar functional groups present on the polymeric chains [173]. In 2020, Sarmah and Karak synthesized a biobased double-network hydrogel with both cationic (Et_3N^+) and anionic ($-COO^-$) groups on the network structure to investigate the removal capacity of the hydrogel towards both cationic dye (MB) and anionic dye (congo red) from industrial wastewater [174]. The hydrogel was synthesized via cross-linking of ECH and MBA on the starch and PAA network using a two-step one pot procedure. The results showed that the hydrogel is capable of removing both cationic and anionic dyes with maximum removal capacity of 133 mg/g and 64 mg/g, respectively due to the presence of cationic and anionic active sites on the network structure. Therefore, this study established the hydrogel as an effective and efficient adsorbent for dye removal.

1.6.6. Biodegradability

To evaluate the biodegradable property of newly prepared hydrogels from an environmental perspective is very much essential in order to minimize the environmental pollution [9]. Therefore, it is considered as one of the important properties of hydrogels in numerous application fields, especially in agricultural. The biodegradability of hydrogel mainly depends on the materials used to prepare the hydrogel. Temperature, pH, humidity, and oxygen content are the important factors that affect the biodegradation

rate of hydrogels [66]. Saengsuwan *et al.* investigated biodegradation behavior of starch/PVA/PAA/natural rubber-based hydrogel by measuring weight loss (%) over time and found that around 72% of sample degradation was observed after 120 days, indicating the prepared hydrogel could be a potential material for slow release of fertilizer in agriculture [175].

1.6.7. Hemocompatibility

Hemotoxicity is one of the factors that limits the use of biomaterials *in vivo* because it raises the amount of free hemoglobin in the blood, thereby inhibiting normal kidney functions [176]. Therefore, investigation of hemocompatibility of newly prepared hydrogel is an important factor in the biomedical field [177]. From this property, the ability of a substance to destroy RBCs can be studied. In order to use newly prepared hydrogel in biomedical applications, the hydrogel matrix itself must have no or a minimum level of toxicity. From the literature, numerous studies have found reporting hemocompatibility of hydrogels. For example, Tan *et al.* developed hydrogel via polymerization of vinyl-functionalized dextran in the presence of vinyl-modified GO and laponite, for controlled drug delivery and the hydrogel was found to have hemolysis less than 5%, indicating good hemocompatibility [165]. Further, Khalil *et al.* fabricate hydrogel composite based on PVA and CMC using CA as cross-linker and attapulgite as NM, for wound dressings [178]. They investigated hemolysis of the prepared hydrogel and observed that with increasing the amount of CA, hemolysis (%) significantly decreased.

1.7. Applications

Besides high swelling capacity, hydrogels possess a wide range of features such as high adsorption capacity, good biocompatibility, stimuli responsive nature, self-healing ability, etc. The existence of numerous properties makes them suitable for various applications such as biomedical, wastewater treatment, agriculture, sensing, health and safety, food packaging, alternative energy, etc. Some of these common applications are briefly described below.

1.7.1. Agricultural

In arid and semi-arid areas, water scarcity is a major environmental issue as low rain falls severely restricts the sustainability of agricultural products in those areas. Moreover, a significant part of the applied fertilizer is lost to the environment via leaching, surface

run-off and volatilization. In order to solve problems like water scarcity and fertilizer loss, researchers have developed hydrogels for agricultural usage which shows a versatile role in outstanding water absorption property, water-retaining ability and SRF property. The use of agricultural hydrogel as soil conditioners can improve simultaneously the water retention capacity together with biological, chemical and physical properties of soil [38]. Further, utilization of hydrogel as a slow-release system enhances the agrochemicals 'utilization efficiency' [179]. In agricultural applications, AA and AM-based hydrogels are most commonly used which are non-biodegradable in nature. As a safe alternative, biobased hydrogels have been considered to substitute the petroleum-based hydrogels and produce biodegradable and eco-friendly hydrogels for agricultural applications. In this view, biobased hydrogels are used as potential substitutes for petroleum-based hydrogels which are ecofriendly, biodegradable, abundant, relatively low cost, etc. [180]. Hence, the biobased hydrogels are extensively utilized in the agriculture sector. For instance, Thombare *et al.* prepared boron-loaded guar gum-based hydrogel to use as a SRF system in agriculture sector [181]. The hydrogel exhibited water swelling capacity of 356 g/g and release of 38% of boron fertilizer within 30 days of incubation, which indicated the controlled release property of the hydrogel along with high water holding capacity. Therefore, the hydrogel could be considered as potential SRF system in agriculture. In 2021, Durpekova *et al.* developed a biodegradable hydrogel by cross-linking CA with cellulose derivatives to utilize it as a soil conditioner in agricultural sector [182].

Besides using hydrogel as soil conditioner and SRF system, they are also used as a soilless medium for cultivation, especially ornamental gardening because of its potentiality to absorb and store a huge volume of aqueous solutions. In addition to these, 3D network structure of hydrogels can provide suitable conditions for plant growth and seed germination. Therefore, hydrogels are widely used as cultivation media which can supply water as well as nutrients to the plant. Currently, there are several reports available on utilization of hydrogel as a soilless medium. For instance, Coa and Li developed activated carbon and agarose-based hydrogel for soilless cultivation of rapeseed seed germination [183]. The prepared hydrogel was tested as biodegradable and safe. Further, they observed that addition of activated carbon, stimulated the germination and plant growth rate. Zhang *et al.* prepared cellulose-based hydrogel in the presence of CNF for soilless cultivation [184]. They observed that the use of hydrogel with suitable

carboxylate contents could promote the seed germination rate of the black sesame cultivar.

1.7.2. Wastewater treatment

Over the last decades, a significant amount of textile dyes, heavy metal ions, pharmaceutical products, etc. are introducing from petroleum, mining, medicinal, printing, and chemicals industries into the environment continuously that are causing water pollution, a serious environmental problem [185]. Among the different techniques, adsorption is considered as the most advantageous due to their high removal efficiencies, ease of operation, wide applicability, economic and flexibility in the design of adsorbents. Using this technique, various adsorbents including activated carbon, silica and fly ash have been applied till date for water remediation. However, their expensive and nonbiodegradable nature limits their practical use in pollutant removal. Recently, biobased hydrogels have emerged as the potential adsorbent for wastewater treatment due to their distinguished features like eco-friendly, cost-effective, high adsorption capacity, etc. [186]. Further, their excellent potentiality to absorb large volume of water within their 3D porous structures along with the presence of chemically responsive functional groups, make them to capture the pollutants from wastewater and to release them under suitable conditions. The properties like high surface area and porosity are important characteristics for hydrogels to capture contaminants from wastewater. Therefore, hydrogels are considered to be suitable for wastewater treatment [187]. Lin *et al.* have prepared cost effective chitosan and calcium alginate-based hydrogel with the incorporation of bentonite for simultaneous adsorption of Pb(II), Cd(II) and Cu(II) ions [53]. They investigated the metal ion removal capacity of the hydrogel under various conditions, and observed maximum removal capacity for Pb(II), Cd(II) and Cu(II) ions up to 434, 102 and 115 mg/g, respectively. The adsorbent also possesses recyclability. Therefore, it is considered as a promising adsorbent for heavy metal ion removal from wastewater. Further, in 2019, Baghbadorani *et al.* prepared CNFs incorporated starch and AA-based hydrogels for adsorption of Cu(II) ions from water [50]. The prepared HNC was found to have an adsorption capacity of 0.957 g/g, while it was 0.736 g/g for the untreated hydrogel.

Besides using the adsorption technique, photocatalytic degradation has attracted considerable attention to deal with toxic dyes in wastewater. In this method, hydrogels combined with photocatalyst such as TiO_2, CdS, Cu_2O, etc. are used to treat dye

pollutants in wastewater. The reports indicate that hydrogels are promising material for dye degradation due to their large surface area as well as the presence of abundant functional groups which assist photocatalyst to react with dye molecules inside the network [188].

1.7.3. Biomedical

Bio-derived hydrogels have also attracted significant interest in biomedical applications such as controlled drug delivery, wound dressing, tissue engineering, etc. due to their excellent properties. As an immerging biomaterial, hydrogels have drawn much more attention as controlled DDS. The stimuli responsive properties, biocompatibility, non-toxicity with similarities with the biological tissues are the key parameters for success of a hydrogel as an efficient drug carrying agent. Along with other biomedical applications, wound dressing by using hydrogels becomes the most competitive research in recent time. Their self-healing, mechanical, and self-recovery properties make them excellent material for wound dressing applications [189,190]. Moreover, in recent years, 3D printing hydrogels have provided an improved platform for utilization of hydrogels in tissue engineering applications. It is becoming a more powerful tool for the development of a biocompatible hydrogel based on natural polymers [191]. There are various reports on the application of biobased hydrogels in the biomedical field. For instance, Wang *et al.* fabricated a chitosan-based HNC by using *in-situ* synthesized magnetic NPs during gelation [192]. Synthesized HNC was used for Adriamycin and Rifampicin drugs to investigate the effect of magnetic NPs on controlled drug release rate by the hydrogel. It was observed that the release rate was also improved by 67.2% after NPs were added. From the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) assay result and cell morphology reports, it was observed that hydrogel showed excellent biocompatibility. Moreover, in 2018, Kouser *et al.* developed a chitosan and AN-based HNC with incorporation of carbon nanotube as the NM [193]. They confirmed biocompatibility, non-toxicity, high modulus and tensile strength of the prepared HNC, indicating the hydrogel's potential for use in tissue engineering applications. Further, Sarmah and Karak developed a mechanically tough hydrogel based on starch and agar for wound dressing application [194]. They synthesized a monomer free hydrogel that is biocompatible and biodegradable in nature. They also studied antibacterial activity and controlled drug release properties of the prepared hydrogel.

1.7.4. Health and hygiene

Hydrogels, especially SAHs, are predominantly used in hygiene products such as female napkins, sanitary pads, baby diapers, etc. as they can retain significant amount of water or biological fluids in their network structure [195]. Petroleum-based PAA hydrogels are the primary polymer used for preparation of SAHs. Due to their non-biodegradable nature, disposed diapers are not easily degraded in the soil, causing adverse impacts on the environment in the form of solid waste. Further, use of AA causes severe skin irritation in babies. Therefore, research works have been performed in the development of sustainable alternative materials for personal care products. The best alternatives contain polysaccharides (like guar gum, starch, cellulose, etc.) and protein-based (like collagen, gelatine, etc.) SAHs. They exhibit properties like safety, biocompatibility, biodegradability, relatively low cost, etc. Therefore, they are widely used as an environmentally friendly and sustainable replacement to various non-renewable petroleum-based materials. Enawgaw *et al.* synthesized a biobased personal hygiene hydrogel using cellulose as the base material via radical polymerization method [11]. It was observed that the hydrogel exhibits WAC of 279.6 g/g and 83.3 g/g in urine solution. Further, Maso *et al.* fabricated a biobased superabsorbent using CNF for potential use in baby diapers [196].

1.7.5. Miscellaneous

In addition to the above-mentioned applications, SAHs are also used in various other applications. As a result of their properties including flexibility, conductivity, thermal stability, etc., they are used in development of energy storage devices such as supercapacitors, batteries, etc. [197]. Recently, hydrogels derived from biomaterials have been explored for food packaging applications due to their antibacterial low-cost, biodegradable, and good moisture barrier properties [56]. Moreover, oil/water separation has also emerged as a promising application of hydrogels. Additionally, they have received significant interest in different areas such as cosmetic formulations, enhanced oil recovery, sensor, etc. Thus, hydrogels have found extensive applicability as advanced biomaterials in the diverse fields of applications.

1.8. Scopes and objectives

It is clear from the state-of-the-art literature that significant works have been carried out in the development of polysaccharide-based hydrogels for various fields of applications. However, the amounts of synthetic monomers used for grafting is still very high

compared to the used biobased raw materials to produce SAHs. Therefore, utilization of biobased components, like IA, starch, cellulose, etc. may provide a unique opportunity for the fabrication of environmentally friendly SAHs. Further, a lot of research has been performed to prepare hydrogel composites and nanocomposites using various inorganic and organic micro- and nano-reinforcing agents. However, relatively very less reports are available on utilization WP derived cellulosic materials like bulk cellulose, CNFs in fabrication of SAHCs and SAHNCs. Since WP is an ideal source of cellulose, it does not require additional physical and chemical treatments in order to remove the lignin and hemicellulose. Besides, it will be advantageous to isolate cellulosic reinforcing agents from WP instead of using fresh plant sources. Therefore, the incorporation of these eco-friendly reinforcing agents will lead to obtaining economical and efficient hydrogels for various potential applications. Further, there is very less literature available on the development of SAHNCs with incorporation of ZnO and CNF based nanohybrid, obtained via eco-friendly and nontoxic approaches. Thus, utilization of biobased materials and WP-derived cellulosic reinforcing materials may pave the way for the development of economical, efficient, and ecofriendly SAHCs and SAHNCs for various potential applications such as agricultural, wastewater treatment, biomedical, etc.

Based on the ideas obtained from the literature survey, the following objectives have been planned for the present investigation.

i) To synthesize hydrogels with high WAC using polysaccharide as a major component.

ii) To use biobased components as much as possible for the synthesis of different SAHs.

iii) To use biobased materials as reinforcing materials in the preparation of hydrogel composites and nanocomposites.

iv) To characterize the synthesized hydrogels by using different analytical and spectroscopic techniques.

v) To study the properties like water swelling, slow release, adsorption capacity, biocompatibility, biodegradability, stimuli responsiveness, etc. of the synthesized hydrogels.

vi) To utilize synthesized hydrogels in different fields of their potential applications.

1.9. Plan of research

In order to achieve the above objectives, the proposed work has been planned as follows.

1. A thorough literature survey has been conducted in the field of biobased hydrogels, NMs and their nanocomposites.
2. Hydrogel matrixes have been synthesized using biobased raw materials such as starch, IA, etc. with the help of literature reports and characterization has been done using different spectroscopic and analytical techniques such as FTIR, TGA, etc.
3. Different properties of the synthesized hydrogels have been evaluated, and the best composition has been chosen for further study.
4. Different cellulosic reinforcing agents (such as cellulosic WP powder, CNF and mCNF) have been obtained via simple and conventional techniques. The plant mediated preparation of CNF/ZnO nanohybrid has also been attempted.
5. Characterization of prepared reinforcing agents and their hydrogels has been performed using various spectroscopic and microscopic techniques such as FTIR, XRD, UV, SEM, XPS, EDX, FESEM, etc.
6. The effectiveness of synthesized hydrogels has been investigated by studying various properties such as water swelling, stimuli responsive swelling, antibacterial, biocompatibility, biodegradability, etc.
7. The best studied SAHs obtained from optimization have been utilized for their possible potential applications such as SRF, seed germination, metal and dye removal, control drug delivery, etc.

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