

REVIEW ON : AGRICULTURAL WASTE BASED
HYDROGELS

**A Project Work Submitted in Partial fulfilment of the Requirements for the
Degree of MASTER OF SCIENCE in CHEMISTRY**

Submitted by

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We GURUDAS GANGULY (2k22/MSCCHE/12) and INDU GAUTAM (2k22/MSCCHE/14) hereby certify that the work which is being presented in the thesis reviewed on “ **Agricultural waste based hydrogel** “ in partial fulfilment of the requirements for the award of the Degree of Master in Science, submitted to the Department of Applied Chemistry, Delhi Technological University is an authentic record of my own work carried out during the period from Aug 2023 to May 2024 under the supervision of

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The matter presented in the thesis has not been submitted by us for the award of any other degree of this or any other institute.

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Gurudas Ganguly(2k22/MSCCHE/12) and INDU Gautam (2k22/MSCCHE/14) has carried out their research work presented in this thesis entitled Certified that ‘**AGRICULTURAL WASTE BASED HYDROGEL** ‘ for the award of Master of Science from the Department of Applied Chemistry, Delhi Technological University, Delhi, under my supervision.

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Acknowledgement

We are incredibly lucky to have had the counsel and support of so many people throughout the project's completion, as it was necessary for its success and outcome.

We would like to thank my project supervisor, DR. Deenan sandhya of Delhi Technological University's Department of Applied Chemistry, for giving us the wonderful chance to work under their capable supervision. Their intelligent and scholarly advice enables me to finish the assignment on schedule.

We are grateful to Prof. Anil Kumar, Head of Delhi Technological University's Department of Applied Chemistry, for his unwavering inspiration.

We are appreciative of and lucky to have the ongoing support, encouragement, and direction from every member of the Department of Applied chemistry ,which helped me in completing this project .

Lastly, but just as crucial, we would like to sincerely thank our family and friends for putting up with our long work hours and for being the inspiration behind our efforts.

GURUDAS AND INDU

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ABSTRACT

The majority of farm wastes are high in cellulose, hemicellulose and lignin. These are basically biodegradable, economical and completely environment friendly. There is vast amount of agricultural waste generated everyday. Superabsorbent hydrogels can be made by extracting nanocellulose using chemical or mechanical methods. When used to agricultural fields as soil amendments, superabsorbent hydrogels serve as reservoirs for water and nutrients. This article explores the potential effects of using superabsorbent hydrogels made from agricultural waste and covers current developments in this field. It also looks for its future prospects like uses in agricultural realm and human health. A comparison is made between the advantages and disadvantages of various existing methods and technologies for hydrogel production and nanocellulose extraction. It is discovered that while physical procedures are more expensive and complex, they are environmentally benign, chemical approaches are often more cost-effective but may endanger ecosystems. Given that these new superabsorbent hydrogels have the ability to decrease irrigation, the economic feasibility of applying them as soil amendments is also covered.



Fig1. Sources of agricultural wastes

INTRODUCTION

One of the biggest global challenges is providing food for the world's fast expanding population

Overuse of chemical fertilisers and irrigation water has been common in recent decades to boost agricultural productivity, particularly in many developing nations. For instance, the majority of China's rice fields receive excessive fertilisation, ranging from 30 to 80% N (Peng et al., 2010). Consequently, Chinese agriculture typically has a low nitrogen usage efficiency (NUE) of 26–36%. Overfertilized nitrogen (N) that is not used by crops in agricultural fields causes eutrophication (Kohler et al., 2006); it also produces N₂O, a well-known greenhouse gas, and acidifies agricultural soils through ammonia deposition. Millions of tonnes of agricultural waste are produced annually, which is a significant obstacle to agricultural intensification. Waste that remains after producing and processing agricultural products, such as grains, dairy products, fruits, vegetables, meat, and poultry, is referred to as agricultural waste. Crop waste (rice husk, wheat straws, sugarcane bagasse), animal waste (animal excreta, dead animals), processing waste (packaging materials, fertiliser cans), and hazardous waste (pesticides, insecticides) are the four general categories into which agricultural waste is divided. The globe produces about 180 million tonnes of bagasse, 203 million tonnes of maize straw, 354 million tonnes of wheat straw, and 731 million tonnes of rice straw annually. According to the Indian Ministry of New and Renewable Energy (MNRE), India produced 500 million tons of agricultural waste, out of which 92 metric tons were burned each year that causes severe environmental pollution by producing a large amount of greenhouse gases (viz., N₂O, SO₂, CH₄) and smoke. These agricultural wastes require a lot of area and energy to landfill, and leachate problems arise as a result (Schiopu and Gavrilescu, 2010). Following harvest seasons, crop leftovers are burned on farms in many developing nations, producing significant volumes of particulate matter, air pollutants, and greenhouse gases (CO₂, N₂O, and CH₄) as well as air pollutants (CO, NH₃, NO_x, SO₂, and volatile organic compounds). There is an immediate need for sustainable agricultural waste management. Large amounts of cellulose, hemicellulose and lignin are present in the majority of agricultural wastes. According recent research has shown that these mostly indigestible polysaccharides can be utilised to create superabsorbent hydrogels, which are hydrophilic polymers with a light crosslinking that can absorb a large amount of water or aqueous solution into their three-dimensional networks. According to Bhattarai et al. (2010), hydrogels, sometimes referred to as hydrophilic gels, are crosslinked three-dimensional polymeric networks that are abundant in

hydrophilic groups. Due to the presence of both physical and chemical crosslinking in their structure, hydrogels have a large affinity to absorb water and organic solvents, up to a thousand times their own dry weight (Hoffman 2012). However, they remain insoluble in aqueous solution. Because of its porous nature, which creates capillary pressure and causes the pores to physically fill with water, as well as osmotic pressure, which is what propels water uptake, hydrogels behave as superabsorber bends. It can also be defined as a polymeric substance that, although not degrading in water, has the ability to swell and hold an adequate amount of water within its structure. Because of their high water content, they have a degree of flexibility that is extremely close to that of natural tissue. Crosslinks between network chains give hydrogels their immunity to breakdown, whereas hydrophilic functional groups connected to polymeric skeletons give them the ability to absorb water.

1.2. SOURCES OF AGRICULTURAL WASTE

1.2.1. CELLULOSE:

With a total production of 1011–1012 tonnes per year, cellulose is the most abundant natural raw. It is an inexpensive, tough, water-insoluble polymer that is biodegradable and renewable that supports the structure of plant, oomycete, and algal cell walls. T. In addition to being the safest substance on the planet and having good mechanical strength, cellulose also offers the advantages of being biocompatible, biodegradable, renewable, and ecologically friendly 61% . A linear chain of β (1 \rightarrow 4) linked D-glucose units makes up cellulose, a polysaccharide in general (Table 2). Its characteristics include being odourless, tasteless, and insoluble in most organic solvents and water . With a high concentration of hydrogen bonds between and among molecules as well as Van der Waals forces, this hydrophilic substance makes dissolving challenging. Cellulose is renewable and widely accessible. The most prevalent natural material is cellulose, which is present in biomaterials like fruits, vegetables, trees, plants, and biowaste. The concept of green and renewable materials is becoming increasingly relevant in research endeavours aimed at developing and implementing ecologically friendly products made from natural raw materials. Materials from agricultural commodities and food waste make up bio-based materials. As a result, bio-based materials address environmental concerns and serve as novel materials in a variety of applications for renewable resources. Commercial sources of cellulose include mainly wood or cotton. However, cellulose can also be extracted from different parts of plants and other sources , that some varieties of wood may have as much as 90% cellulose, and that natural sources like cotton may contain as much as 98% cellulose. However, it has been

discovered that some materials, such the insides of mango pits and tomato leaves and 10.9%, respectively. Because they securely return to the natural carbon cycle through a simple decomposition process in the presence of decomposers, cellulose and many cellulose products are not harmful to the environment. Among its distinctive qualities are its hydrophilicity, potential as a sorbent, non-toxicity, ease of chemical modification, good mechanical qualities, and, last but not least, its safe disposal after use. Despite the fact that cellulose has a wide range of applications and uses, the vast amounts of cellulose-based waste materials that come from industrial or agricultural processes are frequently seen as useless. One potential use of the vast number of renewable and biodegradable raw materials that are accessible from many sources is as adsorbent in a variety of forms, such as raw or modified cellulose or ACs, to remove contaminants from water, such as dyes, phenols, metals, pesticides, etc. Because of its limited adsorption capability, natural cellulose can also be changed as an adsorbent. The removal of different contaminants from modified cellulose has been observed to be significantly greater than that of commercial ion exchange resins and other naturally occurring absorbent materials in many circumstances. Limitations with cellulose arise in relation to dissolution. Few people know about cellulose dissolved in the majority of organic solvents including water. Nonetheless, scientists typically employ various cellulose dissolving solvent systems, such as ionic liquids (ILs), NaOH/urea and NaOH/thiourea because they are readily available and easy to use. ILs are challenging to manageable and intricate. The NaOH/urea solvent system is the most widely used one, as it is inexpensive, practical, simple to make, and capable of speeding up the pace at which cellulose dissolves at low temperature.

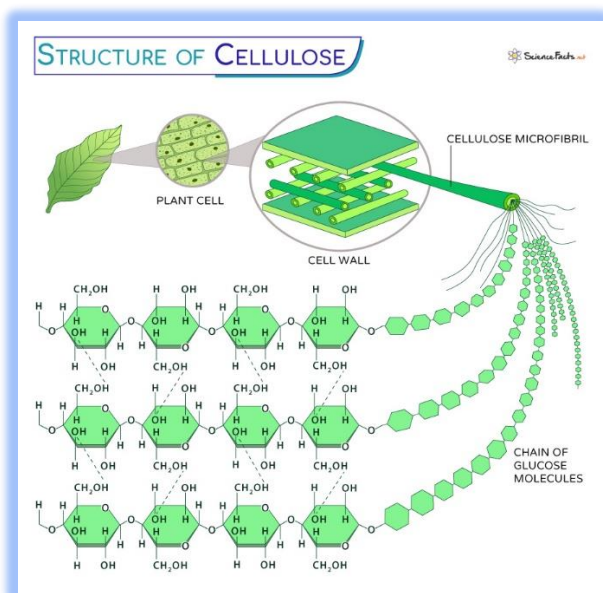


Fig2. structure of cellulose

CELLULOSE DERIVATIVES :

Although cellulose is an excellent starting material, its application is limited because of its difficult disintegration. A chemical reaction into different derivatives is another method to increase the applications. The unique cellulose hydrogen bond is what allows hydrogels to keep their structure when crosslinking chemicals are used. As a result, this subtopic provides further information regarding the synthesis, characteristics, and uses of cellulose derivatives.

Hydroxypropyl Methylcellulose (HPMC):

The thickening, gelling, and swelling qualities of hydroxypropyl methylcellulose (HPMC) make it a popular cellulose derivative in controlled release applications. Additionally, its easy compression, swelling properties, and tolerance of high drug concentrations all contribute to its benign nature. Because of its high biocompatibility, HPMC can be a thermosensitive natural polymer. It can also produce a transparent, colourless hydrogel with good stability, viscosity, and texture modification. In order to adjust the permeability features of the films, the addition of HPMC to the micro fibrillated cellulose film as a pore maker. The 218 result demonstrates HPMC's potent reaction with micro fabricated cellulose in the film, where it may create a hydrogen bond at the surface of the film. HPMC is employed in scaffold engineering applications through the process of chitosan crosslinking). They demonstrate how HPMC crosslinking with chitosan can offer structural support and morphological aspects for the repair process subsequent to the promotion of cellular qualities. Additionally, HPMC was employed as a composite hydrogel in scaffold engineering applications by. They demonstrate how the HPMC composite hydrogel can shorten the duration of the procedure, lessen the invasiveness of osteoplasty surgery, and result in uniform arrangement of cells .

Hydroxyethyl Cellulose (HEC):

HEC is a cellulose ether with good hydrophilicity, water solubility, ease of manufacturing, and biocompatibility and biodegradability. Because the HEC chains have a lot of reactive -OH groups on them, they can be altered to create new materials with better characteristics. HEC is a non-ionic cellulose ether that is easily manufactured using natural cellulose as a raw material and is readily soluble in water. Owing to its benefits, HEC is also appropriate for use in vitro release and bacteriostasis applications in medicine. The use of HEC in the creation of hydrogels revealed strong diffusion of water molecules into the network, indicating a large development of pores in the hydrogel network. Furthermore, a study demonstrates that HEC hydrogel has a high and controllable encapsulation for in vitro release. Because of its biocompatibility and non-immunogenicity, HEC is widely employed as a stabiliser, thickening, coating, medicinal, and cosmetic .

Carboxymethyl Cellulose (CMC):

Water-soluble cellulose derivatives, or CMCs, are widely used in the biopolymer sector. It is created by partially substituting a carboxymethyl group for the hydroxyls 2, 3, and 6 of the cellulose backbone. Since cellulose is a naturally occurring biopolymer that is inexpensive and readily available on Earth, it may be appealing as a beginning material. In addition, CMC possesses the qualities of solubility, biodegradability, and biocompatibility. Using carboxymethylation, CMC is made in a non-aqueous monochloroacetic acid/soda solvent mixture to determine the degree of substitution. Potential applications for CMC-based hydrogel include medication administration, wound healing, enzyme immobilisation, and adsorbents. Tissue engineering, medication administration, wound healing, and antibacterial activity can all be achieved with CMC/nanoparticles hydrogel. The enhanced hydrogel performance in CMC hydrogel is demonstrated by the addition of nanoparticles. Excellent mechanical, electrical, optical, and chemical capabilities of nanoparticles can be used to enhance CMC hydrogels. The CMC that is derived from pineapple leaves demonstrates a potent hydrogen connection between the components and an effective carrier for papain immobilisation. Since CMC can be readily extracted from biomass wastes, bagasse and empty fruit bunches (EFB) are two more biomass wastes that have been used to extract CMC. CMC has special qualities due to each biomass waste, including strong swelling capacity, outstanding optical characteristics, and excellent absorption/ adsorption. Another benefit of using different biomass wastes with high methylation groups is the ability to create CMC-based hydrogels. Additionally, CMC has been employed as a crosslinking agent, demonstrating an improvement in toughness and self-healing in cases where the hydrogen bond was created via a simple ion-exchange method. Due to the regulation of dye molecule diffusion in the CMC hydrogels, a combination of monomer and CMC demonstrated high adsorption and removal of dye in the other application. In cases where the combination of metal/CMC shown greatest removal, the addition of metals to CMC also demonstrates excellent dye adsorption. The degree of CMC substitution increases as NaOH concentration increases because CMC can be diluted in water, which enhances CMC's capacity to dissolve in water.

Hydroxypropyl cellulose (HPC) :

Through an ether connection on the three reactive hydroxyls present on the unit monomer of cellulose, propylene oxide functions as a replacement for cellulose. White sensitivity and turbidity have enhanced because to the radiation approach used to prepare hydrogel from HPC utilising γ -radiation. A study demonstrates the interaction between alkynyl-HPC, which produced larger pore walls and high water absorption, and metals with HPC, which effectively

removes dyes from their aqueous solution. The carbon–carbon triple bond that makes up the alkynyl group is readily soluble. In order to preserve the network structure of hydrogels, it can create additional hydrogen bonds with HPC .

CELLULOSE DISSOLUTION

It is necessary to dissolve cellulose in order to expand. Numerous solvent solutions, including ionic liquids, LiOH/urea, NaOH/urea, and NaOH/thiourea, have been investigated with the purpose of dissolving cellulose. The combination of urea and alkali in cellulose dissolving is more efficient than using just alkali, and the cellulose's homogeneity varies depending on the solvent system. To guarantee that the cellulose is uniform throughout the solution preparation process, it is imperative to dissolve the cellulose using various solvent systems.

NAOH/UREA:

One solvent system that attracts interest is sodium hydroxide/urea (NaOH/urea) because of its affordability, ease of use, low toxicity, and environmental friendliness [45]. Under specific conditions (low temperature, restricted range of concentration), cellulose can be dissolved in NaOH/urea. Chen et al. claim that the interaction happens when cellulose forms an alkali-and urea-shaped hydrogen-bond-induced inclusion complex. Past studies have demonstrated that the temperature of the solvent, the molecular weight of the cellulose, its crystallinity, the rate of stirring, and the duration of stirring all affect cellulose dissolution.

It is known that cellulose exhibits low degree polymerization and poor crystallinity when exposed to cold temperatures (–10 to –20 °C) and minor concentrations of NaOH (7–10 wt%). The hydrogen link between the chains of cellulose polymer is broken at lower temperatures by the OH[–] anion. In order to stop chains from reaggregating, Na⁺ also helps with the process of breaking bonds and structuring the surrounding water .The reason for cellulose dissolution is because hydrated NaOH attracts cellulose chains more by creating an inclusion complex, which is a new hydrogen bond. However, because of its instability, aggregation could lead to the destruction of the cellulose inclusion complex. Therefore, the –OH groups in cellulose molecules can create inter- and intramolecular bonds that can be broken by NaOH when it hydrates with water.

Ionic liquids (ils):

Salts that melt below the boiling point of water are known as ionic liquids (ILs), and they are divided into weakly coordinated anions and cations. Because they are soluble in water and organic solvents, stable, polar, non-flammable, recyclable, and non-volatile, ILs are regarded

as environmentally beneficial solvents. Since ILs are seen to be costly due to their high production costs and time consumption, they typically combine with chemical substances to create alternatives that minimise utilisation. Due to its exceptional dissolving qualities, ease of handling, and ability to dissolve cellulose without derivatization, ILs have emerged as the new direct dissolving method for cellulose in recent years. In order to enhance cellulose solubility, ILs dissolve it by creating a hydrogen bond with hydroxyl and ether oxygen.

1.2.2. LIGNIN

Lignin is the second most abundant plant polymer on Earth and one of the three main components that make up the cell walls of naturally occurring lignocellulosic plants. About 30% of the organic carbon in the biosphere is made up of lignin, which is the only scalable renewable feedstock made of aromatic moieties. It makes up roughly 30% of softwood and 20–25% of the mass of hardwood. In addition to its natural abundance, lignin is a significant byproduct of the pulp and paper industry. Of the 70 million tonnes of lignin produced, only around 2 percent have been burned in pulping mills to recover heat and replace fossil fuels. Due to its natural qualities, including compatibility and environmental friendliness, lignin has been highly sought after for creating high-value functional materials rather than burning.

Phenyl propanol units make up the high molecular weight polymer known as natural lignin. Three distinct phenyl-propane monomers, known as sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol, make up the structure of lignin. The ratios of lignin's three monomers govern the kind of configuration that exists within the lignin molecule, which in turn determines the lignin's degree of branching and reactivity. Three phenolic sub-structures—syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units—are where the monomers transfer to.

Numerous functional groups, including hydroxyls, carboxyls, carbonyls, and methoxyls, are present in these subunits and can be used as active sites for further chemical modification and lignin utilisation. Under biorefinery conditions, bioengineering has the potential to facilitate lignin recovery and chemical transformation by modifying its structure and/or incorporating atypical components. It has been demonstrated that increasing the lignin monomer composition's flexibility helps to improve extraction efficiency.

Genomics-based bioenergy crop development and genetic biosynthesis pathway modification have yielded diverse lignin feedstocks with distinct characteristics for coproduct creation [9]. According to a recent study, agricultural and forestry waste may create more than 1.3 billion tonnes of biomass yearly. In the interim, a large number of important industrial chemicals are refined aromatic compounds derived from petrochemical feedstocks. Since lignin is a plentiful

renewable feedstock made up of aromatics, it has a lot of potential for producing aromatic compounds, which are used in industrial processes .Furthermore, because of its polyphenolic properties, lignin has been promoted as a sustainable biomaterial. Since lignin has a high degree of functionality (rich in phenolic and aliphatic hydroxyl groups), it could be a great option for chemical reactions and alterations in the creation of new bio-based products. Over the past few decades, lignin chemical modification has been the focus of many important investigations and research projects. The performance of the resulting bio-composite has been greatly reinforced by the changes made to the hydroxyl groups in lignin. Furthermore, petroleum-derived polyacrylonitrile (PAN) polymer is currently used in the production of the majority of carbon-based materials and compounds. By taking the place of PAN as an inexpensive carbon fibre precursor, lignin has the potential to revolutionise the conventional carbon fibre business .

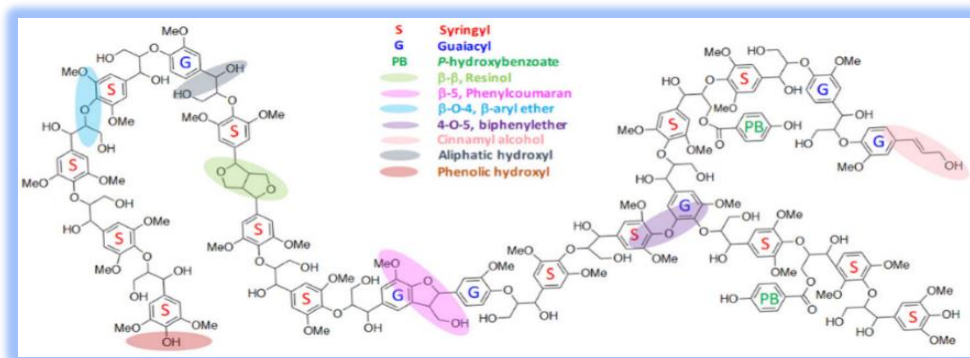


Fig3. **Detailed structure of lignin**

LIGNIN BASED HYDROGELS (TECHNICAL SOURCE OF LIGNIN)

Lignin has a tremendous deal of potential for usage in functional hydrogels because it is the sole aromatic polymer. Generally speaking, pulping processes yield three distinct types of lignin: Kraft lignin, liginosulfonate, and organosolv lignin. Lignin-based hydrogels have been made using three lignin monomers, cress, and biomass pretreatments. Because of the high frequency of condensed structures (C\C connections) and low aryl ether linkages (β -O-4) during the pulp cooking process, kraft lignin is significantly less reactive than the other two kinds of lignin .For instance, liginosulfonate has been utilised as a dispersion agent for both single and mixed powder slips and has been shown to have greater water solubility than Kraft lignin .

Kraft lignin:

The kraft process is based on the employment of a combination of alkaline cooking chemicals, sodium hydroxide (NaOH) and sodium sulphide (Na₂S), known as white liquor's principal reagent, at high temperature (140–170°C), with the goal of removing the lignin from the lignocellulosic materials.

The technical lignin comes from the delignification process, which leaves behind a black fluid that contains oxidised inorganic compounds, various organic components, and degraded lignin that may have come from the lignocellulosic material employed as feedstock. Six After being separated from the kraft black liquor by acidification, the kraft lignin produced by the kraft pulping process is extremely condensed, including a large number of C-C bonds and strong ether linkages. Owing to the chemical agents utilised in the kraft pulping process, kraft lignin could contain some contaminants Such as sulfur .Because sulphur is venous, these impurities in its structure may inhibit catalysts from working or possibly make its use impractical. Six Because -aryl linkages break during cooking, kraft lignin contains a high concentration of phenolic hydroxyls. During the delignification process, oxidative circumstances can lead to the creation of quinone and catechol structures, as well as an increase in carboxylic groups. The ash and carbohydrate content of kraft lignin is minimal.5. In addition, it possesses a low molecular weight, high polydispersity, and aliphatic thiol groups. Several, studies have been conducted in response to the industry's assertion that, as cellulose pulp output increases, more lignin kraft is created and the industry is unable to use all of the black liquor produced.

Lignosulfonate :

It is the lignin that is extracted from pulp made with sulfite. During the pulping process, lignin is destroyed by acid hydrolysis reactions in a water soluble sulfonated system created by a combination of alkaline earth metal sulfite that performs the delignification of wood. The lignin is broken down into a sulfonated compound during the sulfite process. This compound has a range of functional groups that give it special colloidal capabilities. Six Compared to kraft lignin, lignosulfonates lignin has a greater ash concentration (about 4-8%), a larger molecular weight, and is soluble in water. It has been applied as cement additives, stabilisers, dispersants, binders, detergents, and adhesives as well as feed components and surfactants.

Organosolv lignin:

By solubilizing the lignin using organic solvents, the organosolv delignification technique seeks to separate the lignin from the carbohydrates in the lignocellulosic biomass. The fact that sulfur-free methods may be achievable for many bioproduct applications, depending on the solvents utilised, is also intriguing. By using the organosolv procedure, lignin can be extracted with high purity, chemical reactivity, sulfur-free, and non-toxic properties. It is dependent upon the state in which it is received prior to treatment. It possesses a low molecular weight, polydispersity, and a homogenous structure that is nearly identical to that of native lignin. Research indicates that heightened severity in organosolv procedures results in a 36–56% decrease in the extracted lignin's molar mass when contrasted with untreated lignin. Furthermore, there is a decrease in the amount of aliphatic hydroxyl groups and an increase in syringyl phenolic units and condensed phenolic structures.¹⁷ Because organosolve lignin is extremely hydrophobic, it is highly soluble in organic solvents and nearly insoluble in water. Organosolv lignin must precipitate in order to be recovered from the solvent; this usually entails adjusting the concentration and pH.

1.2.3. HEMICELLULOSE

The third most prevalent natural polysaccharide found in plant materials is hemicellulose. The primary components of plant materials are cellulose, hemicellulose, and lignin. Between 20% and 30% of the weight of the lignocellulosic biomass is made up of hemicellulose. Hemicellulose has shorter chains than cellulose, with 500–3000 sugar units instead of 7000–15,000 glucose molecules per polymer. Hetero polymers, also known as matrix polysaccharides, are made up of several polysaccharides with various chemical bonding patterns to form hemicellulose. Hemicellulose is weak and has an amorphous, random structure. Pentose and hexose are the primary units of polysaccharides. Xylose, mannose, galactose, rhamnose, and arabinose are the units of pentose and hexose. Hemicellulose is extracted from wood products using a variety of techniques, including steam treatment, acid pretreatments, alkaline extraction, liquid hot-water extraction, and ionic liquid extraction. The hemicellulose can be extracted using these techniques. Sulfuric acid pretreatment, on the other hand, can yield more dissolved sugars from the broken down products. Froschauer and associates have employed the ionic liquid method to extract very pure hemicellulose, even though the hot-water process has the ability to split the acetate group from hemicellulose. Hemicellulose extraction is a well-researched and widely used alkaline approach. The rationale is that, depending on the product you are targeting, the alkaline technique may preserve hemicellulose integrity the longest. Regarding the hydrogel and film, it might be crucial to

separate the hemicellulose from the biomass using the alkaline approach.

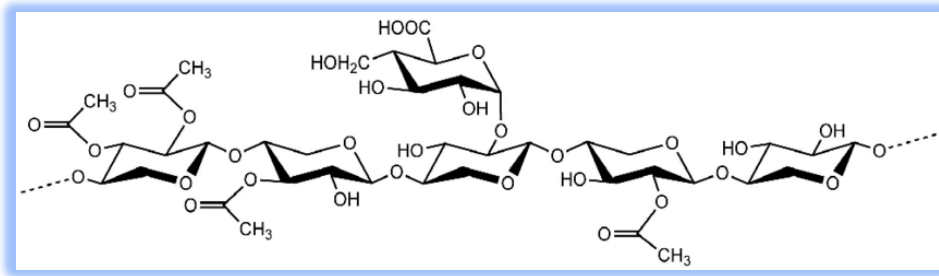


Fig4. Structure of hemicellulose

HEMICELLULOSE HYDROGELS AND ITS DERIVATIVES

One of the most plentiful natural resources is hemicellulose, which is found in large amounts in plant tissue as lignin and cellulose's cell wall filler. Hemicellulose and lignin form a chemical link that allows hemicellulose to attach to cellulose via van der Waals force. Hemicelluloses offer enormous promise in a number of industries. Owing to their unique characteristics, including a large amount of hydroxyl groups in their structure, hemicellulose can be modified through a variety of chemical reactions and physical interactions to create a wide range of products, including packing films, coatings that are water- and oxygen-resistant, and ether-based reactions. Several types of hemicellulose from various plants, including birch wood, Bamboo, straw etc. are used to prepare hydrogel. Hydrogels with hemicellulose as its foundation have been made using a variety of monomers. Among these monomers are methacrylic acid, maleic acid, and acrylic acid (AA). One significant monomer that is frequently employed in the creation of functional hydrogels is acrylic acid. It is well known that acrylic acid works very well as a monomer to produce hydrogels. Indeed, hemicellulose extracted from the majority of plant species can react with acrylic acid quite quickly. Peng et al.'s study shows that hemicellulose recovered from bamboo using an alkali technique (10% KOH) copolymerized with acrylic acid in the presence of a cross-linker. Various ratios of AA/XH and MBA/XH were utilised to examine the impact of the networks. The findings demonstrated that the hydrogels in their as-prepared state were pH-sensitive and could absorb 91–822 times their own weight. The hydrogels also exhibit reversible on-off switching behaviour in water-ethanol or acetone solutions, as well as in acidic-basic solutions. In a different investigation, the hydrogel created by grafting acrylic acid onto hemicellulose's backbone had an exceptionally sensitive pH and a porous structure resembling a honeycomb.

The biodegradability test was also carried out in the interim. Because the hydrogel contains hemicellulose, it can actually deteriorate.

1.3.PREPARATION METHODS OF HYDROGELS

1.3.1.PHYSICAL CROSS-LINKING METHODS :

The advantages of not requiring cross-linking agents and their relative simplicity of manufacture have led to a rise in interest in physical or reversible gels. These compounds have an impact on both the requirement for the removal of target substances prior to application and the integrity of target substances (e.g., cells, proteins, etc.). A lot of attention is currently being paid to the careful selection of hydrocolloid type, concentration, and pH, which can result in the development of a wide variety of gel textures, especially in the food business. The different techniques listed in the literature to produce hydrogels with physical cross-links are:

Heating and cooling a polymer solution :

Heating and cooling a solution of polymers When hot solutions of gelatine or carrageenan cool, physically cross-linked gels are created. According to Funami et al. (2007), helix formation, helice association, and the formation of junction zones are the causes of the gel formation. Above the melting transition temperature, carrageenan is present in hot solution in the form of a random coil. It transforms into a stiff helical rod after cooling. Double helices further combine to form stable gels in the presence of salt (K^+ , Na^+ , etc.) as a result of screening the sulphonic group's (SO_3^-) repulsion (Figure 3). In certain instances, block copolymerization can also be achieved by merely heating the polymer solutions to produce hydrogel. Hoffman (2002) cites polyethylene oxide-polypropylene oxide and polyethylene glycol-polylactic acid hydrogel as a few examples.

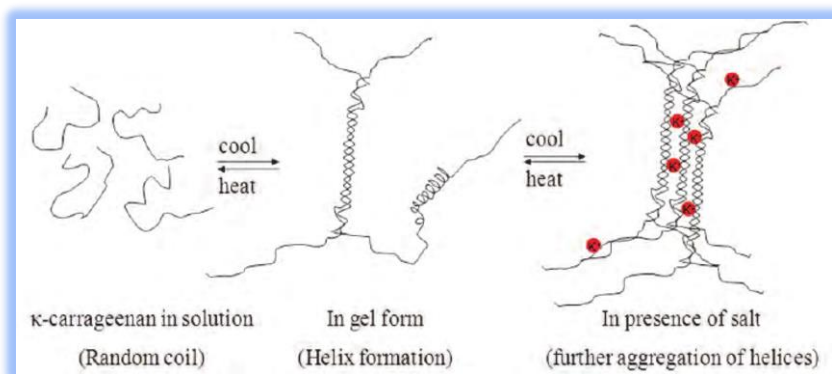


Fig4. crosslinking due to heating and cooling

Complex coacervation:

By combining a polyanion and a polycation, complex coacervate gels can be created. This method's basic idea is that, depending on the concentration and pH of the corresponding solutions, polymers with opposite charges will cling to one another and form soluble and insoluble complexes (Figure 5). Coacervating polyanionic xanthan with polycationic chitosan is one instance of this (Esteban & Severian, 2000; 2001; 1999). Positively charged proteins below their isoelectric point are more likely to bind with anionic hydrocolloids to produce polyion complex hydrogels.

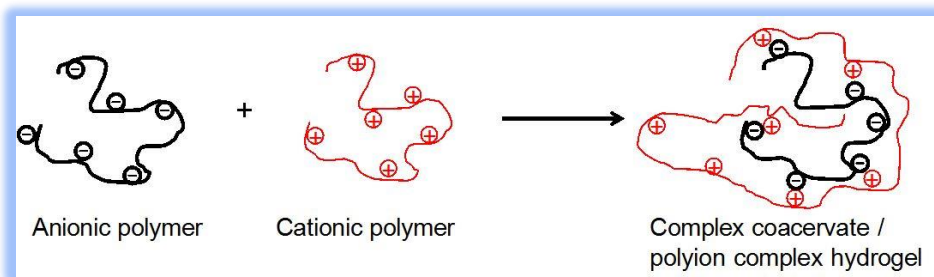


Fig5. complex coacervation

Ionic interaction

Di- or tri-valent counterions can be added to ionic polymers to create a cross-link. The theory of gelling a polyelectrolyte solution (Na^+ alginate $^-$) with a multivalent ion of opposite charges ($\text{Ca}^{2+} + 2\text{Cl}^-$) is based on this technique (Figure 4). Other instances include hydrogels of chitosan and dextran, chitosan-polylysine, and chitosan-glycerol phosphate salt.

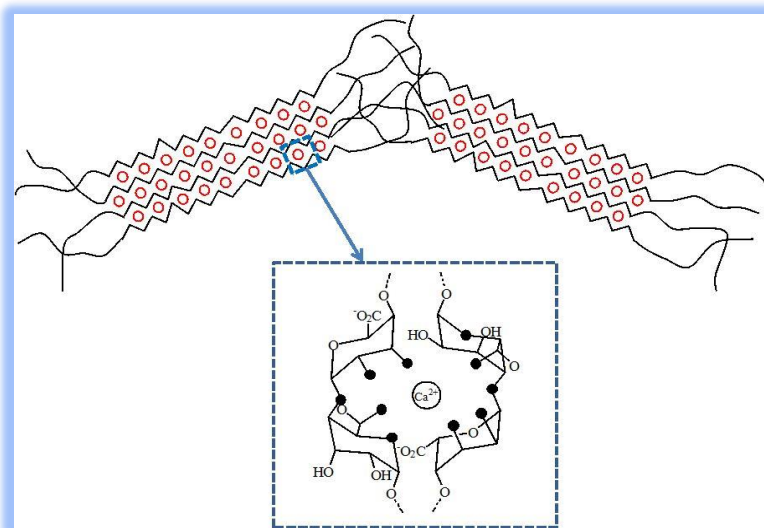


Fig.6 ionic interaction

Hydrogen bonding

Lowering the pH of an aqueous solution of polymers containing carboxyl groups will provide an H-bonded hydrogel. A hydrogen-bound CMC (carboxymethyl cellulose) network created by distributing CMC into 0.1M HCl is an example of such a hydrogel. The process entails substituting hydrogen in the acid ++++++ for the sodium in CMC. Polymer with anionic properties To encourage hydrogen bonding, use a poly ion complex hydrogel solution or a cationic polymer complex coacervate. An elastic hydrogel is created as a result of the hydrogen bonding causing a decrease in CMC solubility in water. Hydrogels containing carboxymethylated chitosan (CM-chitosan) can also be made by cross-linking in the presence of polyfunctional monomers or acids.

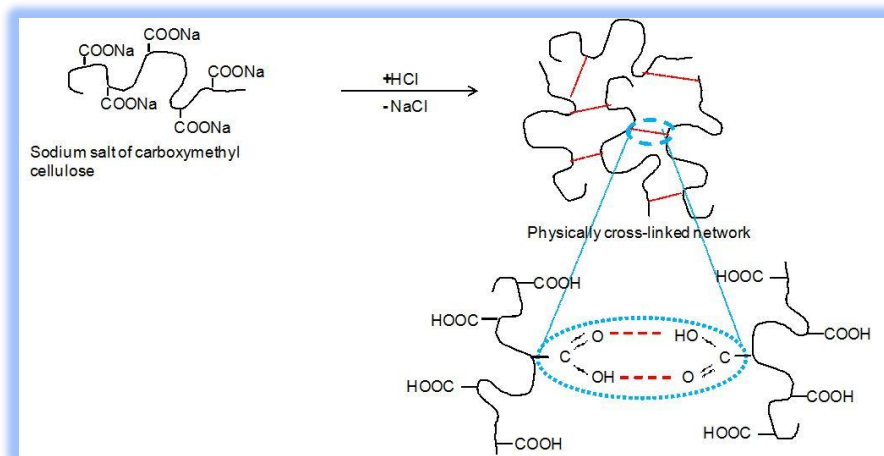


Fig7. Crosslinking due to hydrogen bonding

Maturation (heat induced aggregation)

Although 3-4% of the structure of gum arabic (also known as acacia gums) is protein, it is mostly composed of carbohydrates (Williams & Phillips, 2006). Following fractionation by hydrophobic interaction chromatography, three primary fractions with various molecular weights and protein contents have been discovered. These consist of glycoprotein (GP), arabinogalactan protein (AGP), and arabinogalactan (AG). Heat treatment-induced aggregation of the proteinaceous components raises the molecular weight, which in turn creates a hydrogel form with improved mechanical and water-binding capabilities. The maturation process is accompanied by molecular modifications that show how a hydrogel with finely organised molecular dimensions can be created. The aggregation of proteinaceous components within the molecularly scattered system found in naturally occurring gum is the regulating feature. As the

gum ages, the protein linked to the lower molecular weight components transfers, resulting in higher quantities of the high molecular weight fraction (AGP). The technique has also been used to treat various gums, including *Acacia kerensis* and gum ghatti, in denture care.

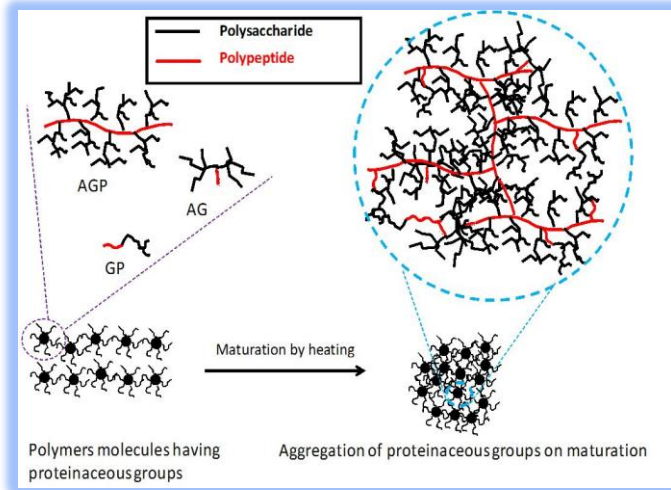


Fig8. Maturation

Freeze -thaaw

Freeze-thaw Another method for creating a polymer's hydrogel is by physically cross-linking it with freeze-thaw cycles. The process involves the structure's microcrystals forming as a result of freeze-thawing. Polyvinyl alcohol and xanthan gum gels that have been freeze-thawed are instances of this kind of gelation.

1.3.2.CHEMICAL CROSS LINKING

Chemical cross-linking is discussed here, which involves grafting monomers onto the backbone of polymers or using a cross-linking agent to link two polymer chains. Natural and synthetic polymers can be cross-linked by reacting their functional groups (such as OH, COOH, and NH₂) with cross-linkers like aldehyde (e.g., glutaraldehyde, adipic acid dihydrazide). There are several ways mentioned in the literature for obtaining chemically cross-linked persistent hydrogels. Other chemical cross-linking methods include IPN (polymerise a monomer within another solid polymer to form an interpenetrating network structure) (2003) and hydrophobic interactions (Hennink & Nostrum, 2002) (incorporating a polar hydrophilic group by hydrolysis or oxidation followed by covalent cross-linking).

Chemical cross linkers :

The process entails introducing additional molecules between polymeric chains to create cross-linked chains (Figure 8). One such example is a hydrogel formed by cross-linking corn starch and polyvinyl alcohol with glutaraldehyde (2008). The produced hydrogel membrane could be used to create fake skin while also delivering nutrition, healing agents, and medications to the site of action. CMC chains can also be cross-linked by adding 1, 3-diaminopropane, resulting in CMC-hydrogel suited for drug delivery through pores (2004). Another example (2002) uses hydrogel composites made of xanthan and polyvinyl alcohol that have been cross-linked with epichlorohydrin. κ -carrageenan and acrylic acid can be cross-linked using 2-acrylamido-2-methylpropanesulfonic acid, resulting in the production of biodegradable hydrogels with potential utility for new drug delivery system.

Click chemistry:

Sharples define click chemistry as specific types of reactions in the presence of a catalyst that are fast and efficient, have excellent biological characteristics, and occur under favourable reaction circumstances. Click chemistry is an important part of polymer synthesis and activation, and it is also an effective and versatile approach for functionalizing compounds. Because of the advantages of click chemistry, it is utilised to produce hydrogels, nanogels, and microgels. It has been served as a substrate for tissue engineering and drug delivery.

1.3.3. GRAFTING

Grafting is the polymerization of a monomer onto the backbone of a premade polymer. Chemical reagents or high-energy radiation treatments activate the polymer chains. The development of functional monomers on activated macroradicals causes branching and then cross-linking.

Chemical grafting:

This method of grafting activates macromolecular backbones through the action of a chemical reagent. This procedure involves grafting starch with acrylic acid using N-vinyl-2-pyrrolidone, as an example. Such hydrogels have good pH-dependent swelling properties and are appropriate for use as a medication and nutrient delivery method in the small intestine.

Radiation grafting :

Grafting can also be initiated using high energy radiation, such as gamma and electron beams. CMC hydrogel is created by grafting CMC with acrylic acid in aqueous solution while being irradiated with electron beams. An electron beam was utilised to start the free radical polymerization of acrylic acid on the backbone of CMC. Water radiolysis product can also be used to extract proton from macromolecular backbones. Irradiation of both (CMC and

monomer) generates free radicals, which can combine to form hydrogel. They proposed the use of an acrylic acid-based hydrogel to recover metal ions such as copper, nickel, cobalt, and lead. They also described the use of hydrogels in dressings for temporary skin coverings.

1.3.4. RADIATION COSS LINKING

Radiation cross-linking is a popular technology since it eliminates the need for chemical additives, preserving the biopolymer's biocompatibility. Furthermore, alteration and sterilisation can be accomplished in a single step, making it a cost-effective technique to modify biopolymers for use in biomedical applications. The process is based on the production of free radicals in the polymer after exposure to a high energy source such as a gamma ray, an x-ray, or an electron beam. The action of radiation (direct or indirect) depends on the polymer environment (i.e., dilute solution, concentrated solution, solid state).

1.4.CHARACTERISATION METHOD

1.4.1 FTIR

Fourier Transform Infrared Spectroscopy, or FTIR, is a helpful method for determining a substance's chemical structure. It is predicated on the idea that a substance's fundamental constituents, or chemical bonds, may typically be activated and absorb infrared light at frequencies characteristic of the many types of chemical bonds. The measured sample's fingerprint can be seen in the ensuing infrared absorption spectrum. This method is frequently employed to compare the hydrogel's structural arrangement with the initial ingredients.

1.4.2 SEM

SEM can reveal details about the composition, surface topography, and other characteristics of the material, including electrical conductivity. In a SEM, the magnification can be adjusted from roughly 10 to 500,000 times across a range of up to 6 orders of magnitude. This effective method is frequently employed to capture the distinctive "network" structure found in hydrogels.

1.4.3 Rheology

The several types of structure (association, entanglement, and cross-links) that are present in the system have a significant impact on the rheological properties. At low frequencies, polymer solutions are essentially viscous and tend to fit the scaling rules $G' \sim \omega^2$ and $G'' \sim \omega$. Elasticity is dominant at high frequencies ($G' > G''$). With a single relaxation period that can be found from the crossover point and that lengthens with concentration, this activity is consistent with Maxwell-type behaviour. It shows that G' and G'' for cross-linked microgel dispersions are

nearly independent of oscillation frequency. The network structure of a variety of hydrocolloids, including chitosan-based cationic hydrogel, seroglucan/borax hydrogel, and others, has been described using this method.

1.4.4. Light scattering

GPC-MALLS, or gel permeation chromatography connected on-line to a multi angle laser light scattering, is a commonly used method to ascertain the characteristics and molecular distribution of a polymeric system. With this method, hydrogel in a polymeric system may be measured. This method is frequently used to quantify the hydrogels of several hydrocolloids, including pullulan, gelatin, and gum arabic.

1.4.5. Other methods

Nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) are the primary techniques used to characterise and measure the amount of bound and free water in hydrogels. Information regarding the exchange of water molecules between the so-called free and bound states is provided by proton NMR. The amount of free water in the hydrogel sample under test can be determined by measuring the endotherm when the frozen gel is warmed up. This is because the use of DSC is predicated on the idea that only the free water may freeze. The difference between the hydrogel test specimen's measured total water content and its computed free water content is then used to determine the bound water. Confirmation of the creation of cross-linked network gel structures of hydrogel is also achieved by thermogravimetric analysis, X-ray diffraction, sol-gel analysis, etc

1.5. IMPACTS ON HUMAN HEALTH AND AGRICULTURE:

1.5.1. HUMAN HEALTH :

Hydrogels have attracted a lot of interest in the medical community because of its special qualities, which include biocompatibility, physically adjustable characteristics, and the capacity to imitate real tissues. Through their numerous uses in healthcare and medicine, hydrogels' effects on human health can be comprehended. Hydrogels have a significant effect on human health because of their many uses in tissue engineering, drug delivery, wound care, and other areas. They are an important tool in modern medicine because of their capacity to imitate genuine tissues and offer controlled conditions for therapeutic actions.

Tissue engineering

In addition to tissue engineering, hydrogels are three-dimensional chemical compound scaffolds with numerous sustainable uses in technical textiles. Thus, a broad range of essential cluster of procedures known as "in-vivo tissue regeneration." Because the patient's own cells

are mixed with the chemical substance in this instance and are controlled in vitro until they may be embedded, the hydrogel fibre functions as a naturally occurring extra-cellular matrix, which subsequently encourages tissue regeneration and cell proliferation. Research on the pseudo-extra-cellular matrix, which is made up of growth factors, metabolites, and other elements, is expanding in the field of medical textiles. This matrix governs tissue structure and facilitates cell proliferation, allowing for the replacement of native tissues that have been inadvertently destroyed or misplaced. Because hydrogels have a large mass and an innate attraction for biomolecules, they make perfect substrates for the covalent or noncovalent confinement of a wide variety of biomolecules. Hydrogel-free biomolecules can be engineered to possess distinct release mechanisms, such as regulated or burst release. Applying external stimuli to hydrogels, such as ultrasound, light, heat, or magnetic or electrical fields, is another method for the on-demand release of biomolecules. Electronic devices that monitor the release of therapeutic chemicals into the body at a suitable time and rate can be combined with these bio responsive hydrogels.

Drug delivery

From the perspective of drug delivery, we typically aim to use the entire set of methods, tools, and procedures to minimise the problems associated with standard medical administration, such as sudden unharnessing and rapid deterioration of the drug's effects over time, especially for prescription medications with short half-lives. Particularly, hydrogel-based smart biomaterials based on fibres will be a very intriguing promise in achieving a sustained and targeted release of prescription pharmaceuticals, each of which will simultaneously increase the drug's own impact and reduce side effects. The researchers noted that silk fibroin from *Natherea Mylitta* and *Bombyx mori* can be readily formed into a three-dimensional scaffold for internal organ tissue engineering. Such an innovation was made regarding the growth of cardiomyocytes, the reaction of metabolic cells, and the spectrum of cell-cell junctions for *Antheraea Mylitta* fibroin, which is remarkably similar to fibronectin. AM silk fibroin enables effective cell attachment during treatment without influencing the cells' sensitivity to external stimuli

Contact Lenses

Soft contact lens manufacturers frequently utilise hydrogels because of their high water content and oxygen permeability.

Comfort: High water content keeps you from becoming too dry and guarantees comfort.

Oxygen Permeability: Preserves eye health by allowing oxygen to reach the cornea.

Prosthetics and Implants

Because of their mechanical qualities and biocompatibility, hydrogels are utilised in a variety of implants and prosthetics.

Breast implants: Compared to silicone implants, hydrogel-filled implants feel more natural. Hydrogels can be utilised in soft tissue implants in order to replace or strengthen damaged tissue.

Eye care

Hydrogels are utilised in ophthalmic applications other than contact lenses, like: Hydrogels can be utilised to fabricate synthetic corneas for usage in corneal implants. medication Delivery: Sustained medication release can be achieved with hydrogel-based eye drops and implants.

1.5.2. AGRICULTURE :

Water-absorbing polymers known as hydrogels have a high capacity to retain water in relation to their bulk. Their ability to enhance soil characteristics, boost crop yields, and improve water usage efficiency has sparked a lot of interest in their application in agriculture. Hydrogels hold great potential as a tool for sustainable agriculture, especially in areas where water is scarce. Their capacity to increase crop yields, strengthen soil structure, and optimise water and nutrient use efficiency can all have a major positive impact on global food security. To successfully integrate them into conventional farming operations, cost, environmental impact, and practical use must all be balanced.

Effective Water Retention and Use

Up to several hundred times their dry weight in water can be absorbed and retained by hydrogels, which then gradually releases the water. Because of this feature, they are especially helpful in dry and semi-arid areas where crop development is restricted by a lack of water. Hydrogels assist in reducing the frequency of irrigation, which saves water resources and lowers irrigation costs by increasing soil water retention.

Reduction of Drought Stress:

When there is a lack of water in the soil, it causes oxygen radicals to be produced, which in turn causes lipid peroxidation and oxidative stress in the plants. Drought stress consequently has several negative consequences on plant morphology, including a reduction in leaf area, a loss of plant height, and eventually leaf damage. Consequently, even in unfavourable weather conditions, the use of hydrogels can act as saving tools for increased plant development and

agricultural yield. Numerous studies have documented the benefits of hydrogel in gardening; additionally, it could enhance the soil's ability to retain water and augment the capacity of permeable soils to store water, hence diminishing the likelihood of plant wilting.

Use as soil amendments

appropriate soil conditioners to a common solution helps to improve the qualities of the soil. Because hydrogel (absorbent polymers) can collect water and release it over time for plant uptake, its application in agriculture is essential. In order to lessen water loss, conserve nutrients in the soil, and lessen the detrimental effects of dehydration and moisture stress on crops, hydrogel polymers are being used as soil additives in agriculture (Gokavi et al., 2018). Hydrogel polymers, in particular, provide a number of benefits when applied to soils, including the ability to: (i) operate as a long-lasting gel by absorbing hundreds of times its own weight in water; and (ii) shield the soil from runoff. Lastly, it has the potential to increase soil microbial activity. (iii) It is efficient in enhancing the performance of soil fertilisers. Yin et al. (2018) examined the biological impacts of polyglutamic acid, an inventive hydrogel polymer component, on maize growth, as well as the enhancement effects of beneficial soil microbes. Utilising this organic polymer has demonstrated its ability to improve soil water conservation, boost maize seedling growth, and raise the number of microbiological bacteria that support plant growth, including Burcholderia, Pseudomonas, and Bacillus. Control seepage by creating membranes in the soil that enhance aeration, drainage, and permeability, control the downward flow of water and nutrients, and shield plants from the harmful effects of salt toxicity.

Hydrogel as a Potting media

Because it is lightweight and easy to handle, hydrogel is becoming a more popular potting media for plants, especially in soilless culture systems. Hydrogel is therefore regarded as a lightweight growing medium that can be utilised to cultivate crops in the present day. Excellent water-holding qualities are a potting medium's most important requirement in order to supply water and nutrients for plant growth. In the 1950s, hydrogel was first employed as a potting media in urban farming. Since then, it has also been utilised in slow-release coatings, as a seed supplement, and to help seedlings form stronger roots. Excellent water-retention capacity was revealed by a poly-acrylamide-co-acrylic acid/silver-coated superabsorbent hydrogel nanocomposite, which may be useful in rainfed agriculture.

Effective watering

Using hydrogel as a soil amendment can lower the frequency of watering because of its ability to retain water in the soil for extended periods of time .It has been demonstrated that using hydrogel in sandy soils helps retain water, reducing the demand for irrigation. The water usage efficiency of growing *Agrostis stolonifera* was enhanced by the addition of 0.4% hydrogel as a soil supplement. Vegetable crops grown on sandy soils benefit greatly from hydrogel treatment, as demonstrated by the results of red sandy loam and alluvial soils. In comparison to untreated soils, plants may get water for almost 1.5–2 times longer.

Methods of Application

There are several ways to use hydrogels: you can mix them into the soil directly, cover seeds with hydrogel, or use them in potting mixes for seedlings. The type of crop, the state of the soil, and particular farming techniques all influence the application technique.

Financial Aspects

Hydrogel products' high cost may prevent them from being widely used, particularly in underdeveloped nations. Higher crop yields, better nutrient and water efficiency, and lower irrigation costs can, however, offset the original expenditure over time.

CHAPTER 2

2.CONCLUSION AND FUTURE PROSPECTS

We know there is enormous amount of agricultural waste that is being generated everyday .Every year more than billions of tons of waste is generated .These waste generated are not being disposed properly due to scarcity of awareness .Often ,either these wastes are burnt openly which result in evolution of green house gases horns the climate crisis or dispose it into the water which demises the quality of water .This article reviews about the hydrogels derived from these agricultural waste .agricultural wastes are highly rich in lignocellulose biomass .cellulose ,lignin ,hemicellulose ,chitosan etc, are the parts of the biomass .these have complex 3d structure due to polymerisation of different functional groups .these biomasses and their derivatives can be utilised to develop hydrogels and super absorbent hydrogels .

over the last decade hydrogels have caught researchers attention due to its profound qualities like water retention or absorbing capacity, biodegradability, non toxicity , swelling ability and other like its sensitivity to stimulate in different conditions .

In recent times scientist have done enormous research and praised its effectiveness in different fields specially on agriculture and human health. Its profound qualities can be magnificently helpful in modern day agriculture like curing drought ,enhance soil quality ,proliferate efficient irrigation and what not. Researchers have also enhanced these hydrogels and broadened their use in medical field. These hydrogels are tremendously efficient in drug delivery, wound healing , tissue engineering ,developing biosensors ,safe cosmetic products etc.

Nevertheless , future looking more promising in area of agriculture and medical field with hydrogels and its sustainability can be long ranged by using agricultural wastes as a source of.

CHAPTER 3

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