

Synthesis of Cellulose-Based Hydrogel from Sugarcane Bagasse and its Application in Water Treatment and Management

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I, Himanshu Meena, Roll No. 2K21/MSCCHE/22, student of M.Sc. Chemistry, hereby declare that the project Dissertation titled “Synthesis of Cellulose-Based Hydrogel from Sugarcane Bagasse and its Application in Water Treatment and Management”, which is submitted by me to the Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Science is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma, Associateship, Fellowship, or other similar title or recognition.

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ABSTRACT

Water is a valuable natural resource on the world, but industrial and human activities are polluting it more and more. One of the essential tasks of the twenty-first century is the development of cheap, environmentally acceptable methods to filter the hazardous wastewater with heavy metals and dyes. Adsorption is a somewhat efficient and cost-effective approach among these. One such promising adsorbent is hydrogels (HGs), which are macromolecular, three-dimensional crosslinked networks of the hydrophilic group that are capable of both adsorbing these dyes and metal ions from wastewater as well as Having the ability to storing and throwing out a considerable volume of liquids, including water; due to this property, they are also used in sustainable agriculture. A lot of academics have recently become interested in cellulose-based hydrogels (CBHs) because of its high abundance, biodegradability, cost-effectiveness, low toxicity, environment-friendliness, and superior adsorption capability. Agricultural waste is frequently composed of cellulose. Using mechanical, chemical, or a combination of these methods, cellulose can be eliminated to produce superabsorbent hydrogels. In this study, we examine the method of extraction of cellulose from sugarcane bagasse using the alkali-acid pre-treatment method. We also estimated the content of cellulose in treated sugarcane bagasse using a UV-Visible optical density (OD) spectrophotometer and characterize both untreated and treated sugarcane bagasse using Thermogravimetric analysis, ATR-FTIR spectroscopy, and Scanning electron microscopy that helps in effective synthesis of cellulose-based hydrogel and exploring the potential effects of using them in water treatment and management.

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CHAPTER 1

INTRODUCTION

Sugar manufacturers produce sugarcane bagasse as a by-product of the juice extraction process. Since just a few commercial uses were initially developed for those enormous volumes of waste, the accumulation of significant amounts of sugarcane bagasse as agricultural waste results in a complex waste problem [1]. About 40–50% of sugarcane bagasse is composed of cellulose, 25% of which is hemicellulose, which is mostly made up of the sugars glucose, xylose, galactose, mannose, and arabinose, 25% of which is lignin, and a smaller amount of wax, mineral, and other chemicals [2]. Hemicellulose and lignin, which act as a cementing matrix, make cellulose fibres less accessible and make the process of isolating cellulose more challenging. Lignin and hemicellulose must be eliminated to effectively separate out cellulose as well as increase the utilisation of the isolated cellulose [3]. Alkaline-acidic pre-treatments combined in two-phase chemical pre-treatments have been shown to be highly effective at removing the components of hemicellulose and lignin [4]. The most prevalent natural polymer, cellulose is also affordable, environmentally friendly, biocompatible, and biodegradable. It constitutes a linear chain comprising β -1,4-linked anhydro-D-glucose units that are 180 degrees out of alignment with one another. The amount of polymerization in the chain ranges from a few hundred to more than ten thousand. In addition, the molecular chains of cellulose include a large number of -OH groups. Because of this property, cellulose can easily be altered to create better and more useful cellulose-based products through chemical or physical cross-linking [5]. A macromolecular polymeric substance known as a hydrogel may swell, absorb, and hold a significant amount of water, minerals, or physiological fluids within its framework. It is made up of 3-D network structures and hydrophilic chains of polymers [5]. Numerous elements, including amorphous, crystallinity areas, porous structure, and net surface area, affect the capacity of cellulose to swell in water. Significant limitations of cellulose hydrogels include absorbing moisture, varying quality, having poor thermal properties, and not working with hydrophobic polymer matrixes [6]. Artificial polymer inclusion

in cellulose hydrogel has been produced for a variety of purposes, including transparency, mechanical characteristics, and swelling activity. The biggest artificial polymer that is both soluble in water and recyclable is poly(vinyl alcohol, or PVA). Because PVA has an appropriate framework that includes a -OH group, which makes it hydrophilic, it is frequently used in industrial settings to increase the mechanical durability of films [7].

In this work, cellulose has been isolated from sugarcane bagasse for the purpose of cellulose-based hydrogel synthesis. Sugarcane bagasse was pre-treated with acid and alkali to separate the cellulose. The amount of cellulose content in treated sugarcane bagasse was obtained by UV-Visible optical density (OD) spectra. Both raw bagasse and treated bagasse were characterized using Thermogravimetric analysis, ATR-FTIR spectroscopy, and Scanning electron microscopy to confirm the successful modification. This study can help the material's properties for hydrogel synthesis as they relate to applications in the water treatment.

CHAPTER 2

LITERATURE REVIEW

One of the most urgent concerns facing all nations in various parts of the world is the treatment and management of water. Fresh water makes up around 3% of the overall water reserve, although about a third of it is currently useable for other purposes [8]. Lakes, rivers, the sea, underground water, fresh water basins, and other water sources are the main ones that can become more and more contaminated by industrial and commercial facilities or human activities [9], [10]. One of the essential challenges of the twenty-first century is locating low-cost, environmentally friendly methods of decontaminating wastewater produced with heavy metals, dyes [11]–[13], pesticides, and oil [14], [15] to stop the depletion of readily available water resources. Along with heavy metals and dyes, one of the most frequent contaminants that negatively affects water sources is radioactive waste, which is a waste product that contains radioactive particles. This waste is frequently created during nuclear processes like nuclear fission. Although such material's radioactivity will progressively decrease, it will happen so slowly, which might have substantial long-term effects on both the vegetation and wildlife [16]. Dyes offer major health risks to aquatic life because they block sunlight from infiltrating water, even in small quantities. This lowers the level of oxygen that is dissolved in the water. On various occasions, dyes have been seen triggering anaerobic digestion, which produces a number of carcinogenic chemicals that later make their way into the food chain through aquatic plants and animals [17]. On the other hand, heavy metal ions provide a threat to human health because of their elevated risk of toxicity and carcinogenicity. The kidneys, neurological system, brain, and circulatory systems can be harmed by these toxins, which are also dangerous to plants, animals, and marine life. This increases the chance of getting cancer and other serious diseases [18]. Scientists from all over the globe are unduly worried about the present-day issues facing the planet, which might be remedied by solar energy-based solutions for converting energy and freshwater generation [19], [20]. Adsorption persists as the most effective and economical method of wastewater treatment for eliminating toxins

from wastewater and organically produced adsorbent materials have already sparked a lot of interest. One of the most promising types of these adsorbents are hydrogels (HGs). A unique class of hydrophilic, physically and chemically cross-linked polymeric three-dimensional network known as a "hydrogel" can contain a large portion of biological fluids and aqueous solvents inside its structures [21]. They can absorb different metal ions and dyes from polluted water with remarkable efficiency. HGs have received a lot of interest recently for their function in removing contaminants from wastewater due to their excellent elimination performance [22]–[25]. The CBHs provide the hydrogel with electrostatic charges that attach it to the structure, which has a twofold effect on the hydrogel's capacity to swell. One element, which results in the polymer chains being longer than they would be in a neutral network due to electrostatic repulsion between charges of the same sign, increases the swelling. On the other hand, a Donnan-type effect leads to more water entering the framework because of the counterions in the hydrogel to maintain macroscopic electrical neutrality [26]. These hydrogels may be formed from chemicals that are found naturally, artificial polymers manufactured from petroleum, or a combination of the two. Natural hydrogels are preferred because they are economical to synthesis, biocompatible, biodegradable, and simple to obtain from a number of sources. These polymeric networks allow for functional group alterations that raise the functional groups' binding affinities for different contaminants in wastewater. Although HGs may also be produced using artificial polymers, natural polymers are more sustainable and ecologically friendly. Because of their great abundance, biocompatibility, exceptional capacity for adsorption, and non-toxicity, cellulose-based hydrogels (CBHs) have been the subject of much investigation. A biodegradable, renewable, biocompatible, and harmless biopolymer called cellulose "Fig. 2.1" is present in the cell walls of nearly all plants. In times of drought, natural polymer hydrogels can slowly discharge water into the earth's soil by soaking up rainwater. They serve as a buffer as a result, increasing the soil's ability to retain water. Utilizing biodegradable biopolymer hydrogels reduces the amount of time that land needs to be frequently watered, improves the ability of the sand to store and soak precipitation, and conforms with the bare minimum environmental protection regulations. Superabsorbent hydrogels are used in agriculture to conserve water resources. Hydrogel could turn out to be a feasible, simple option for increasing agricultural yield in times of water scarcity. Hydrogels may absorb and store irrigation

and precipitation by using both capillary and gravity water, which lessens deep percolation. Agricultural hydrogels are advantageous for the environment since they gradually degrade over time without leaving behind any harmful traces in the environment or on plants. As a result, increasing sustainable agricultural production in dry areas will be possible by using hydrogel as a conditioner for the soil. In this literature review, we analyse a number of current research publications, and we explore deeper into the application of hydrogels in the effective management of water in agricultural use, including the elimination of pollutants such heavy metal ions and dyes present in wastewater.

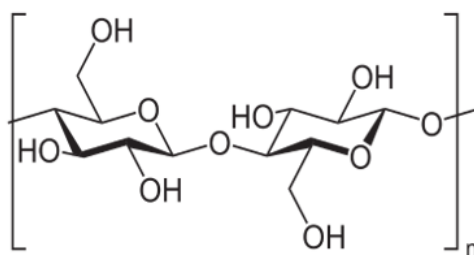


Fig. 2.1. Cellulose [β (1→4) linked D-glucose units]

2.1. HYDROGEL

Wichterle and Lim originally created the hydrogel in the 1960s [27]. There are at least two phases of it. A 3-D structure is a solid phase, whereas water is the dispersion phase [27]–[31]. There are several ways to categorise hydrogels, including (i) the technique of synthesis, (ii) the kind of monomer(s) or polymer(s) employed, and (iii) the ionic charge. Based on the technique of synthesis, polysaccharide HGs are split into two subtypes: (a) physically (reversible) crosslinked hydrogels and (b) chemically (permanent) crosslinked hydrogels [12]. It is now well recognised that hydrogels can be produced via a number of methods, such as physical entanglement, radical, frontal, graft copolymerization, cross-linking, hydrogen bonding, and ionising radiation [32].

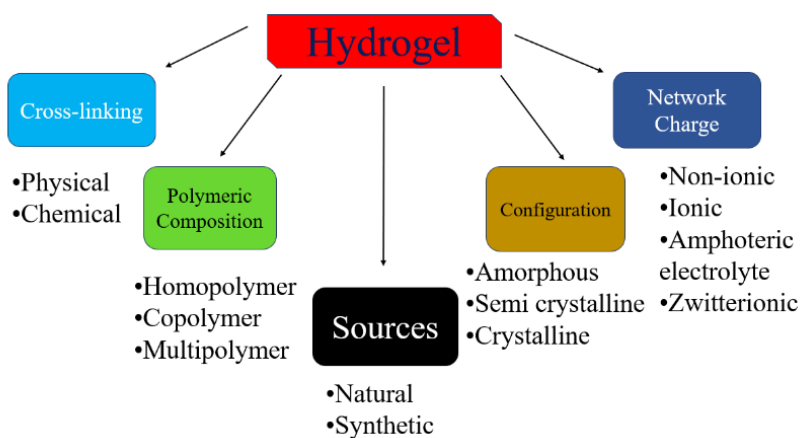


Fig. 2.2. Classification of hydrogel on different basis

Classification of hydrogel based on various factors is represented in “Fig. 2.2”.

Two categories of hydrogel can be distinguished based on their origins-

- Natural – Polypeptide based (such as gelatin, collagen) [33] and polysaccharide-based (such as cellulose, starch, alginate, and agarose) [34]–[37] and
- Synthetic – Petrochemical-based (such as polyacrylic acid, methacrylic acid, vinyl acetate, and polyethylene glycol) [38]–[41]

Synthetic HGs are stronger mechanically and more hydrophobic than natural HGs. Since their improved mechanical strength increases their lifespan or shelf life, synthetic HGs are chosen [42]. Based on the electric charge's presence or absence in the cross-linked chains, Four classifications can be used to describe different CBHs:

- Ionic (anionic and cationic)
- Non-ionic
- Zwitterionic (Each repeating unit contains both positively charged and negatively charged ions)
- Amphoteric electrolyte (both acidic and basic groups) [38]

Depending on their polymeric composition, HGs can be divided into three types:

- Homopolymer - A single kind of monomer, known as a homopolymer, is employed to create the HGs polymeric web network.
- Copolymer - Copolymeric refers to a 3D network that has a minimum of two distinct monomer units and a minimum of one hydrophilic component.
- Multipolymer - An HGs network arrangement holds the two synthetic and/or natural macromolecules that are individually cross-linked and comprise multipolymer interpenetrating hydrogels made of polymers together.

Depending on configuration:

- Crystalline
- Semi-crystalline
- Amorphous

2.2. SYNTHESIS OF CBHs

The excessive use of fossil fuels and materials that are not biodegradable has resulted in a number of issues, which has caused scientists to turn their attention to recyclable and environmentally friendly substances. A wide range of industries, including tissue engineering, agriculture, drug delivery, food packaging, and wastewater treatment, currently using biopolymers [43]–[50]. Similar to this, biopolymer-based hydrogels, like Cellulose-Based Hydrogels, have improved efficiency, excellent solubility in organic solvents, bigger surface area, availability, affordability, enhanced adsorption power, being biodegradable, simplicity in production, and recyclability, making them the best candidates for dye and heavy metal removal via adsorption [51]. Moreover, CBHs are a dependable option for wastewater treatment due to their high hydrophilicity [52]–[55]. Developing a proper CBHs is the fundamental and most crucial step in developing an effective adsorption process. Cellulose Based Hydrogel are typically derived from cellulose (i.e., native/pure cellulose and bacterial cellulose), its derivatives (ether derivatives: methylcellulose, ethylcellulose, hydroxyethyl methylcellulose, hydroxypropyl

cellulose, carboxymethyl cellulose (CMC), etc.; ester derivatives: acetate trimellitate, acetate phthalate, hydroxypropyl methyl phthalate, hydroxypropyl (such as polyelectrolyte complex, interpenetrating polymer networks and blending with other polymers) [51], [56], [52]. Under aqueous conditions, hydrogels are constructed from hydrophilic groups such as -OH, -COOH, -NH₂, -CONH₂, and -SO₃H or a hydrated polymer network. First, hydrogels are made chemically, either in a single process or over the course of several phases. The polymerization method and parallel crosslinking that join numerous monomers are always included in the one-step procedure. In a number of steps, the polymer molecule's reactive group is created. Most hydrogels are created from artificial polymers with a porous structure, which enables them to hold large amounts of water. It is suitable for slow-release applications. The use of hydrogel in agriculture is expanding as a result of how well it controls the release of nutrients, liquids, herbicides, and fertilisers. There might be enough fertiliser in the hydrogel to support the plant's growth. Growing a plant with a longer fertiliser and water retention time might be a simple strategy. Because of their renewability, biocompatibility, and biological properties, biomass resources have been noteworthy materials in hydrogel manufacturing in recent years. To create cellulose-based hydrogels, cotton linter pulp has been used as a hydrogel material with just one crosslinking agent [57]. In order to store a significant quantity of water in its porous network, a stable three-dimensional Hydrogel web framework created by crosslinking the individual polymer chains is required. Because cellulose contains hydrophilic functional groups like hydroxyl (OH), it can create both chemical and physical crosslinks. Depending on the ingredients and manufacturing processes, various interactions are seen in CBHs, including (i) electrostatic interactions between small cations and cellulose, (ii) electrostatic interactions between polycations and cellulose, (iii) H-bond or hydrophobic interactions between polymers and cellulose, (iv) self-assembly, (v) coordination complex crosslinking, and (vi) covalent crosslinking [51], [58].

2.2.1 Physical Path of Crosslinking

However, the use of chemical-free crosslinking agents makes the physical crosslinking process—held by weak connections like interaction due to H-bonding, ionic interactions, the interaction between hydrophobes, π - π interactions, and interaction due to van der Waals weak forces—often more advantageous for environmentally friendly and non-toxic HG synthesis [57], [59]–[65]. Because of their high porosity, which increases their ability of soaking more contaminants, minimal sensitivity to pH, ease of restoration (being a reversible process), and absence of adsorption capability reduction which is caused by a probable crosslinker reaction, as in the chemical procedure [51], physical crosslinked CBHs are widely used for adsorption purposes despite having poor mechanical properties [66]–[68]. Additionally, because hydrogel is an edible polymer, physical crosslinking builds hydrogel structures without harming living things [69].

A. Freeze–Thaw

One of the physical techniques employed for the production of HGs is crystallisation utilising the freeze-thaw method [70]. The freeze-thaw technique crystallises the polymer by lowering the number of chain spacing in the polymers, allowing the chains to orient and connect to form a network model. This procedure involves freezing high-volume liquids or restricted solutes [71], [72]. Low molecular weight solutes or bulk liquids that crystallise on cooling are used in the freeze-thaw procedure. This results in a reduction in inter polymer chain gap, an increase in polymer concentration, and the arrangement and combination of polymer chains to form the interconnected network framework of a hydrogel. High porosity in HGs is made possible by the space left by melting crystals during the thawing stages of freeze-thaw cycles [72], [73]. The covalent contact and hydrogen bonds used in this technology hold the interconnected network structure together. By altering the polymer concentration, the number of freeze-thaw rounds, the freezing and thawing intervals, and the freezing temperature, these HGs' mechanical

properties may be changed [74]. Due to their improved elastic qualities over those produced using chemical techniques, high-grade materials manufactured by the freeze-thaw process have gained attention worldwide [75]. This procedure results in the development of biocompatible and non-toxic polysaccharide-based HGs (such as cellulose, Carboxymethylcellulose, etc.) [76]. The features of polymer gels are improved by the freeze-thaw method of hydrogel synthesis while maintaining their biocompatibility, renewability, and non-toxicity. Additionally, the freeze-thaw method is a helpful technique for the creation of gels, which illustrates the interconnection of hydrogen bonds, due to the negative consequences of the chemicals for covalent crosslinking [73], [77], [78]. Hemicellulose is effectively transformed into a hydrogel via a freeze-thaw process, improving its thermostability, stiffness, and crystal structure. It produced a structure with more rigidity, a property with greater stability, and a high degree of crystallinity [79]. It is clear that a greater frequency of freeze-thaw cycles affects hydrogel microstructure analysis and properties, such as decreasing their porosity. For example, Freeze-thaw procedures are used to create PVA (poly vinyl alcohol)/CMC HGs, which are then used to capture heavy metal ions like Ag^+ , Ni^{2+} , and Cu^{2+} , and Zn^{2+} [70].

B. Self-Assembling

Since no crosslinkers are needed for preparation in self-assembling method, scientists are fascinated by the potential application of self-assembled CBHs. In the process of synthesising the constituent monomers into fibrils through non-covalent contacts (interactions deriving from van der Waals forces, H-bond interactions, electrostatic interactions, and π - π stacking interactions), the fibrils entangle into a dense web network, producing self-assembling HGs [80]. By adjusting the concentration of the constituent monomers, these Hydrogel mechanical characteristics can be altered. Forming HGs can absorb poisonous dyes and metal ions from polluted water. By using layer-by-layer depositing technique i.e. coating on filter sheets, they can also be utilized to treat greasy effluent [81]. Cationic guar gum (CGG) and TEMPO (2,2,6,6 tetramethylpiperidine-1-oxyl)-oxidized cellulose nanofibers (TOCN)

can instantaneously form HGs as soon as they come in contact with each other [71].

C. Instantaneous Gelation

Following the one-step procedure, the instantaneous gelation method is one more option to generate HG immediately [82], [83]. Magnetic chitosan-based HG beads (m-CS/PVA/CCNFs), consisting of carboxylated cellulose nanofibrils (CCNFs), amine-functionalized magnetite nanoparticles, and poly (vinyl alcohol) (PVA) blended chitosan, have been prepared by the instantaneous gelation method as adsorbents for Pb(II) [71], [74].

D. Reconstitution

Ionic liquid is frequently used as a solvent in the reconstitution method for cellulose-based composite hydrogels. The synthesised HGs are held together by an effective intermolecular hydrogen bond, which gradually increases the strength of the bond. For instance, biodegradable collagen/cellulose HG beads (CCHBs) have been prepared by reconstitution from a 1-butyl-3-methylimidazolium chloride ([C4mim] Cl) solution that can potentially be used to adsorb both dyes and heavy metals [75].

E. Inverse Emulsion Technique

When water droplets are dispersed in oil (the continuous phase: paraffin oil) using a suitable stabilizing agent (such as non-ionic surfactant Triton X-100) [51], the phenomenon is known as a "water-in-oil emulsion". To leach the drops and deposit a permeable film, the system is subsequently put through a phase inversion in a coagulation bath. This mechanism is widely known as the inverse emulsion technique [51]. For example, HGs based on sodium

carboxymethyl cellulose and acrylic acid were prepared by inverse emulsion polymerization using potassium persulfate as an initiator and N,N'-methylenebisacrylamide as a crosslinker [71], [76].

F. Ionotropic Gelation

By electrostatically interacting two ionic species, at least one of which must be a polymer, the ionotropic gelation (IG) process enables the synthesis of nanoparticles and microparticles [14]. Ionotropic gelation is also utilised to create cellulose nanocrystals and alginate-based HG beads, which can be used to adsorb organic dyes [77].

2.2.2 Chemical Path of Crosslinking

For greater mechanical strength, chemical crosslinking is preferred over physical crosslinking, and this can be accomplished by using particular functional groups contained in the crosslinking agents. To do this, a chemical crosslinking agent must be added, creating powerful bonds between molecules via covalent and electrostatic forces of contact. Due to the smaller size of the pore and stiffness of the polymer chains, the crystallinity, however, adversely affects the adsorption capability and swelling ratio [66]. The amine, carboxyl, and amide groups of the cross-linking agents are covalently joined to the hydroxyl and carboxyl groups of cellulose [84]. Furthermore, crosslinking agents and higher crosslinking densities interact with some of the binding sites in the adsorbent, necessitating striking the equilibrium within upholding the essential mechanical properties and enhancing the adsorption capacity. [26], [66].

A. Crosslinking by Chemical Reaction

In this, the functional groups in the molecules of polymer or the crosslinking chemical substances and polymer join collectively to form the

link. A covalent bond is used to join a polymer with -OH (like cellulose and its derivative products) and -NH₂ (like chitosan, proteins) groups with a crosslinker that has an -CHO group (aldol formation) [71]. HG formation for polymers with hydroxyl groups requires specific conditions, including a low pH, a high temperature, and the use of methanol as a quencher, while Protein-based HGs can form under standard conditions [25], [85]–[87]. Due to their accessibility and affordability, glutaraldehyde, acetaldehyde, formaldehyde, and epichlorohydrin are common crosslinkers for CBHs [25], [71], [88]. As an illustration, eco-friendly CBHs beads have been created from CMC utilizing an epichlorohydrin (ECH) crosslinker in an inverse suspension crosslinking mechanism, in which the ether linkage is formed between ECH and CMC, resulting in high porosity [51]. More specifically, it is believed that the presence of a number of carboxylate anions (-COO) in the interconnected system of hydrogel beads is what causes the hydrogel to have a porous structure because these anions not only contribute to expanding the HG network but also increase the size and number of its pore spaces, allowing for more metal ions to attach [89]. Similarly crosslinking processes occur in polymers with amine (-NH₂) and ester (-COO-) functionalities, producing Schiff bases by both addition and condensation reactions [90]. Hydrogels can be created by crosslinking polysaccharides using 1, 6-hexamethylene diisocyanate, citric acid, epichlorohydrin (ECH), divinyl sulfone, and numerous other substances. These substances are employed to make sure that a specific polymer or functional group forms a web of connections to produce hydrogels [91]. Ge et al. also prepared a high-performance composite hydrogel (cellulose/poly-ethylene imine (PEI)) by grafting hyperbranched PEI onto cellulose chains using an ECH crosslinker [92]. The hydrogels shown outstanding ability to remove Cu²⁺ ions.

B. Crosslinking by Polymerization

The chain growth polymerization method, which entails three processes involving initiation, propagation, and termination [56], is used to produce a large amount of CBHs. One of the many types of polymerization processes

that is frequently used for the creation of HG is free radical polymerization because it has a more quickly synthesising approach, ease of use pursuant to various circumstances of reaction, a broad temperature range, and is affordable [71], [93]. A free radical is formed from the initiator, such as potassium persulfate (KPS), tetramethylene-diamine (TEMED), ammonium persulfate (APS), etc. [51], for the initiation phase when specific circumstances in terms of sunlight, temperature, pressure, and radiations are present. A three-dimensional network framework is randomly created when the polymer chain expands during propagation, the crosslinker engages with the growing chain, and the polymerization is then stopped by combination or disproportion [25], [56], [66]. A novel fluorescent luminous lignin-based hydrogel made of cellulose nanofibers and carbon dots (CDs) was produced utilising free radical polymerization [94]. Ning et al. [95] synthesized an HEC-co-p(AA-AM)/TA (HEC: hydroxyethyl cellulose, and AM: acrylamide) hydrogel by the grafting of AA and AM onto HEC, followed by modification with TA.

C. Crosslinking by Radiation

It also entails a polymerization process that doesn't require a catalyst or chemical to act as a crosslinker. It generates various forms of radiations to crosslink the polymer chains rather than the chemical crosslinker used in the previous polymerization method. Consequently, it is a free of waste synthesis method that is also ecologically friendly. [25], [66]. It was successful to create methyl hydroxyethyl cellulose hydrogel by using gamma radiation and adding poly (ethylene glycol) (PEG) [96]. The radiation crosslink hydrogel is produced for use in agriculture either by extremely energetic irradiation or by chemically initiating free radicals. The use of gamma radiation has been highlighted as a promising radiation-induced method that can create hydrogel with excellent water absorptivity and high capacity for water retention for a number of polymeric substances [97]. A popular cellulose derivative created using gamma irradiation is CMC-Na [60].

2.3. Cellulose Nanocrystal (CNC) based Nanocomposite Hydrogels

The cellulose fiber found in plant cell walls is employed for the preparation of cellulose nanocrystals (CNCs), which are nanocrystalline components of cellulose biopolymers. The essential characteristics of cellulose nanocrystals include high mechanical durability, hydrophilicity, biological compatibility, nontoxic nature, minimal density, and the capacity for simple modification. CNCs have been used as reinforcing materials in the creation of nanocomposite hydrogels with the goal of enhancing hydrogel performance. The physical attributes of cellulose nanocrystals are influenced by the supply of cellulose and the process of extraction techniques. The hydrogel's tensile strength and tensile modulus were considerably increased by adding 5% CNC to the hydrogel matrix. Both strength and modulus decreased when the CNC particles accumulated at higher concentrations. The CNC-alginate composite hydrogel beads have been developed as an adsorbent for eliminating dye from wastewater discharges. The results demonstrated that the cellulose nanocrystal CNCs acted as both methylene blue (MB) dye binding sites and hydrogel reinforcing components [98].

2.4. Properties of Cellulose-Based Hydrogels

Cost-effectiveness, non-toxicity, biodegradability & biocompatibility, etc. are only a few of the standard attributes of CBHs “Fig. 2.3”.

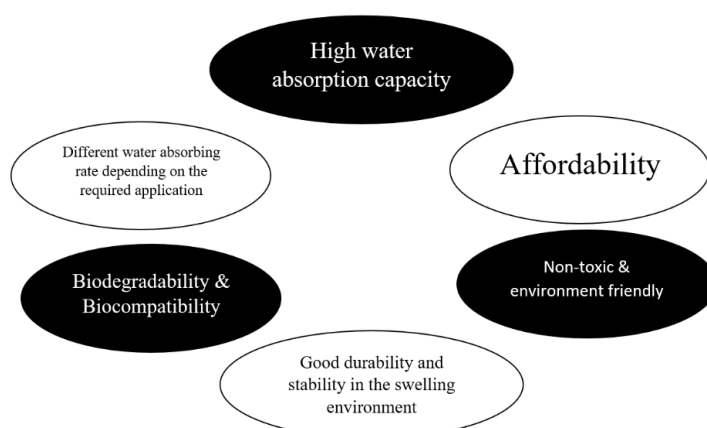


Fig.2.3. Properties of CBHs

The abundance of hydrophilic functional groups in cellulose and its derivatives, such as the -OH, -CO-, and -CHO groups, makes it easy to make hydrogels with interesting shapes and properties. Here, we'll examine CBHs' advantageous traits, including their receptivity to stimuli, mechanical toughness, and ability to heal themselves.

2.4.1. Stimuli-Responsive CBHs

Stimuli-responsive CBHs are highly useful in biomedical applications, especially for drug delivery, because of their unique capacity to suddenly expand or shrink in response to outside stimuli [99]–[101]. In addition to biological/biochemical stimuli like glucose, the environmental stimuli's which includes pH, temperature, redox, light, solvent composition, electric and magnetic fields.

2.4.2. Mechanical Properties

Investigation has been done extensively on the mechanical properties of CBHs, including mechanical rigidity, flexibility, and toughness. Strength was commonly connected with transparency and, like transparency, was affected by the level of separation of phases. For example, it was found that hydrogels with smooth surfaces, more homogeneous designs, and smaller pore dimensions had increased durability [102]. In comparison to conventional single-network HGs, double-network HGs and nanocomposite HGs usually showed greater durability and hardness [103], [104]. In comparison to conventional single-network HGs, double-network HGs and nanocomposite HGs usually showed greater durability and hardness. To achieve better structural performance, dual cross-linked hydrogels, including physical-chemical hybrid cross-linked hydrogels [102] and dual physically cross-linked hydrogels, have been developed [105]. While physical cross-linking helps the viscoelastic and healing properties, chemical cross-linking places in these HGs networks may preserve the flexibility of the HGs.

2.4.3. Self-Healing Properties

Self-healing HGs, also known as self-repair or self-recovery HGs, were created in response to the inherent capacity of some living tissues, like skin, bones, and muscle tissues, to heal themselves after suffering damage. The shape, framework, and functioning of HGs with self-treatment powers can naturally and substantially repair loss (such as being sliced in half). Auto-rehealing HGs and biodegradability have received a lot of attention due to their potential uses in smart wearable devices, tissue development, biomedicine, artificial body parts, hemostatic materials, etc., as well as due to their transparency. Since self-healing HGs typically contain either mechanically strong or quick self-healing qualities but not both, creating HGs with both characteristics is still a great challenge. Designing and creating self-healing HGs that combine dynamic covalent and noncovalent connections into a polymeric network is one approach.

2.5. Application of CBHs

Due to the appealing properties of cellulose and its hydrogels, such as biocompatibility, biodegradability, non-toxicity, aimed and regulated discharge, and tailorability, they are potential candidates for a wide range of purposes in medication delivery, healing wounds, wearable devices/biosensors (smart materials), treatment of waste water, the agricultural sector, etc. [106]. With a specific focus on its use in the fields of treatment of wastewater and efficient use of water in the field of crop watering, the current review aims to give a thorough examination of the technique's applicability.

2.5.1. Application of CBHs for Wastewater Treatment

The toxicity of water by organic pollutants has been one of the most significant issues facing humanity [107]. Oil and petroleum byproducts from oil

leakage incidents, textile industry dyes, and heavy metals from industries are some of the impurities that are most frequently found in wastewater today “Table 2.1”. Numerous of these toxins are known to be dangerous or cancer-causing to humans and have been shown to have negative impact on the planet and its inhabitants as well. Among the heavy metals that is especially hazardous to the environment is mercury. Since they do not biodegrade, heavy metals like mercury and cadmium are linked to a variety of diseases and physical deformities [39]. Furthermore, the presence of artificial colours may irritate the skin, which can cause serious injury to people by impairing their kidneys, reproductive system, liver, brain, and central nervous system, among other organs [108], [109]. They are consequently classified as dangerous and carcinogenic chemicals. Polycyclic aromatic hydrocarbons (PAHs), which are organic compounds made up of many aromatic ring structures, are durable in nature due to their chemically resistant structure. Therefore, they are known as mutagenic, carcinogenic, and toxic substances [110].

Table 2.1. General categories of water contaminants [25], [111].

Generation	Nature	Example
Physical	Color	Dyes, pigments
	Suspended or floating matters	Sand, wood chips, paper, etc.
Chemical	Organic	Plastic, tar, pesticides, oil, etc.
	Inorganic	Nitrates, phosphates, heavy metals, fluorides, etc.
Biological	Pathogenic	Bacteria, Viruses, worms, etc.

There are three categories of wastewater treatment techniques: physical, chemical, and biological processes “Fig. 2.4”.

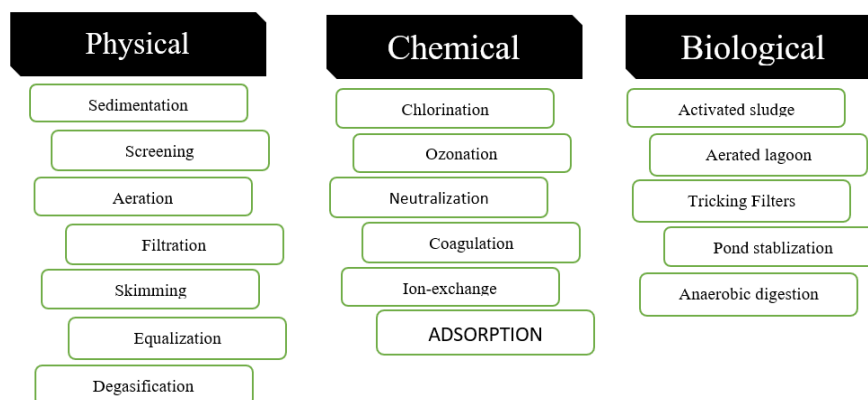


Fig. 2.4. Wastewater treatment techniques

Considering its numerous advantages, including ease of utilisation, practicality, insufficient generation of undesired by-products, excellent and quick sorption capacity, and lack of manufacture of undesirable byproducts, adsorption is believed to be the most efficient approach out of those mentioned above [112]. It is becoming more and more common to employ cheap materials as sorbents for eliminating organic pollutants from wastewater [113].

2.5.2. Adsorption Mechanism

It is essential to have a thorough understand of the mechanisms that supports adsorption as well as the methods used to remove different pollutants utilising various cellulose-based hydrogels so as to enhance the adsorption effectiveness of cellulose-based hydrogels. The hydrogel functional group, adsorbent properties, the chemical composition of pollutants, and experimental variables (such as solution pH, initial pollutant concentration, the coexistence of metal ions, temperature, etc.) all play a significant role in all of the interactions that result in the typical adsorption by CBHs [51], [66]. Although mixes of numerous other interactions with electrostatic interaction have been reported in other adsorption techniques, electrostatic interactions are among the most common adsorption process involved in the removal of dyes and heavy metals by cellulose-based hydrogel [89], [92], [114], [115].

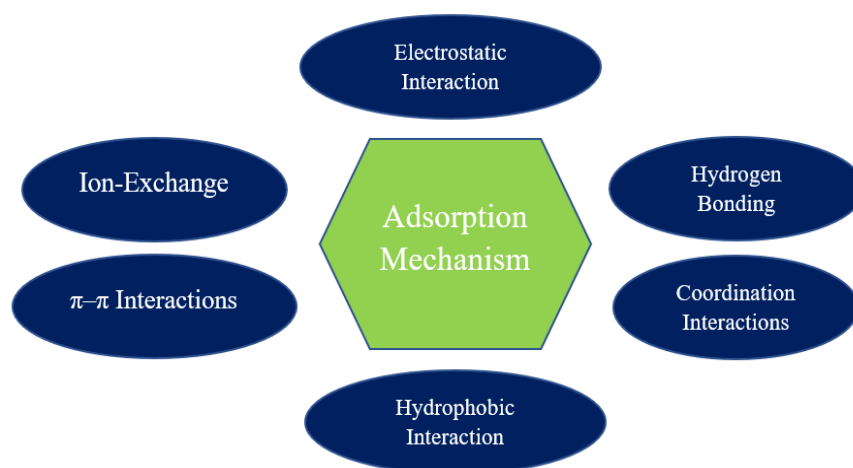


Fig. 2.5. Adsorption mechanism of dyes and heavy metals by cellulose-based hydrogels

A. Electrostatic Interactions

Electrostatic interaction, which occurs whether molecules are identically charged (as in cation-cation or anion-anion interactions) or oppositely charged (as in cation-anion contacts), is the association of charged units. For cellulose-based hydrogel to get rid of ionic contaminants through electrostatic attraction, the surface of the adsorbent must have a charge counter to that of every ion which have to be adsorbed. Depending on the chemical makeup and kind of the contaminants, specific functional groups are added to the cellulose-based hydrogel to enable it to supply an opposing charge to the desired ions [66]. The development of ionic species on the external layer of the adsorbent is also significantly influenced by the pH of the solution [116]. HGs based on the fusion of nanoparticles were interlinked with advantageous electrostatic forces in various studies. These HGs displayed amazing abilities to spontaneously revive themselves and provide reusable characteristics [117]. Numerous studies have suggested that the adsorption of heavy metals and ionic dyes in various HGs is driven by electrostatic forces [118], [119].

B. Ion Exchange

The method of transferring ions among a substance that is insoluble and a liquid (water) (adsorbent) is known as ion exchange. Undesirable soluble ions (ions that are negatively or positively charged) from an aqueous solution are eliminated, and substitutes are discovered on the outermost layer of the adsorbent containing ions that have the same charges. In an ideal ion exchange process, the total number of charged particles discharged from the adsorbent's outermost layer equals the number of ions absorbed by the adsorbent particles [19]. Ion exchange is a very effective method, notably for the elimination of dangerous contaminants from wastewater, such as dyes and heavy metals. This process lowers the level of toxic load by transforming toxins into recyclable forms, leaving behind less dangerous elements in their location, or facilitating future discharge through decreasing the hydraulic flow of the channel that transports poisonous materials. The ion exchange technique also has the capacity to extract contaminants from distillate [118]. Similarly, Ion exchange techniques have been used to remove dyes from aqueous solutions [59], [81], [119].

C. Hydrogen Bonding

.Hydrogen bonding, a particular kind of dipole-dipole interaction, is caused by the electrostatic pull between a positively charged atom of hydrogen and a stronger electronegative atom (such as Nitrogen, Oxygen, Fluorine, etc.) or cluster that are covalently bound. When treating wastewater containing dyes, functional groups with oxygen, such as carboxylic acid (-COOH) and hydroxyl (-OH), participate in the formation of hydrogen bonds with pollutants (dyes) [71], [120]. The adsorption of MB (Methylene blue) on a cellulose-based hydrogel showed the relationship between the electronegative Nitrogen atom in the MB (Methylene blue) molecule and the Hydrogen atom in the carboxylic acid (-COOH) and hydroxyl (-OH) groups of Hydrogel [58].

D. Hydrophobic Interactions

The term "hydrophobic interaction" refers to the contact between hydrophobes and water molecules. Because of poor van der Waals attractive forces, lengthy chains of carbon combine to generate hydrophobes, non-polar compounds that are incapable to interact with molecules of water [121]. Insignificantly dissolved substances in water also demonstrate a potent attraction to hydrophobes. In order to remove non-polar contaminants from aqueous solution, such as pigments, disperse dyes, organic compounds, etc., hydrophobic interactions are created during wastewater treatment [122]. Additionally, for the onset of chemical processes, the hydrophobic domain offers a physical crosslinking point with better mechanical stiffness. Prior to the creation of macromolecular 3D polymer networks, the reaction continues with the synthesis of other polymeric chains [117]. One of the primary adsorption procedures for the insoluble organic contaminants into cellulose cryogels is hydrophobic interaction [123].

To remove contaminants from aqueous solutions, cellulose-based hydrogel is usually treated with both hydrophilic and hydrophobic functional groups. Through electrostatic, H-bonding, and/or ion-exchange interactions, the hydrophilic portion of functional groups attracts soluble ionic pollutants, whereas the hydrophobic portion aids in the adsorption of water-insoluble pollutants [124], [125].

E. Coordination Interactions

A coordination interaction is a covalent bond in which one atom distributes both electrons. When wastewater ions that are positively charged (heavy metal ions and/or ionic dyes) are eliminated using a coordination approach, cations are then adsorbed on the outermost layer of the adsorption material. Atoms in functional groups with lone pair electrons (such as oxygen and nitrogen) in exterior orbitals undergo attraction to cations [51]. Coordination interactions are a type of interaction that can happen together with others like ion exchange and electrostatic interactions. At low pH, the adsorbent surface's H^+ ions are replaced by metal ions from the solution, and these

positively charged heavy metal ions have a strong attraction for negatively charged electrons. In dye molecules, various metal ions as well as Nitrogen & oxygen atoms are often adsorbed on coordination bonds of ion-exchanged functional groups (hydroxyl).

F. π - π Interactions

In an aqueous medium, the " π - π " interaction, a non-covalent link, mediates interactions between the different parts of the adsorbent and adsorbate. Numerous chemical properties, like as boiling temperature, chemical bonding, biomolecular and molecular crystallography, the structure of neighbouring molecules, etc., are significantly influenced by interactions among molecules [70]. In a normal " π - π " contact, interactions in an aqueous medium occur because at least a single of the molecules possesses an electron-rich group or an electron-deficient group [51]. The surface functional groups of the adsorbate and adsorbent as well as the pH of the solution's media have an enormous effect on the π - π interaction [126]. According to these functional groups and the pH of the solution, the adsorbate and adsorbent molecules serve as an electron-donor or electron-acceptor, resulting in the creation of various interactions (electron-donor-acceptor, electron-acceptor-acceptor, and electron-donor-donor) [51], [67].

2.5.3. Factors Affecting the Adsorption Capability of Cellulose-Based Hydrogels "Fig. 2.6"

A. Crosslink Density

The largest adsorption potential is frequently produced by a low crosslink density for cellulose-based hydrogels, and inversely [127]. There is an average or minimal value of crosslink density that has to be achieved to avoid mechanical breakdown or full disintegration of the adsorbent substances [128].

B. Initial Concentration of Pollutant (ICP)

As ICP in wastewater rises, more adsorbate molecules are produced in the same amount of liquid and adsorbent material [129]. More molecules of adsorbate link to the adsorbent's sites of activity, increasing its capacity for adsorption. This increases the concentration gradient's driving force, accelerating the dispersal of dyes or heavy

metals onto the adsorbent sites [13], [51]. Nevertheless, some recent studies found that when pollutant concentration spiked adsorption efficiency decreased [74], [130].

C. pH at the Point of Zero Charge

When the pH is below pH_{PZC} , protonation has increased the H^+ level of the aqueous solution, polarising the outermost layer of the adsorbent positively. The positively charged surface of the adsorbent and anions as a result interact strongly electrostatically. The aqueous solution is deprotonated, creating a negatively charged surface that interacts with cations, when $pH > pH_{PZC}$ [131]–[133]. When ions precipitate in Hydrogel, protonation and deprotonation mostly take place at various functional groups such as $-COOH$ [89] or $-NH_2$ [74], [134]. Every metal ion has a pH range where the best adsorption effectiveness is observed. At a solution's basic pH, cellulose-based hydrogels is more effective at adsorbing heavy metal ions. Metal ions react with the additional $-OH$ groups in an aqueous media at pH values above 7.0 to form metal hydroxides, which obstruct the pathway of adsorption and reduce the potential for adsorption of hydrogels.

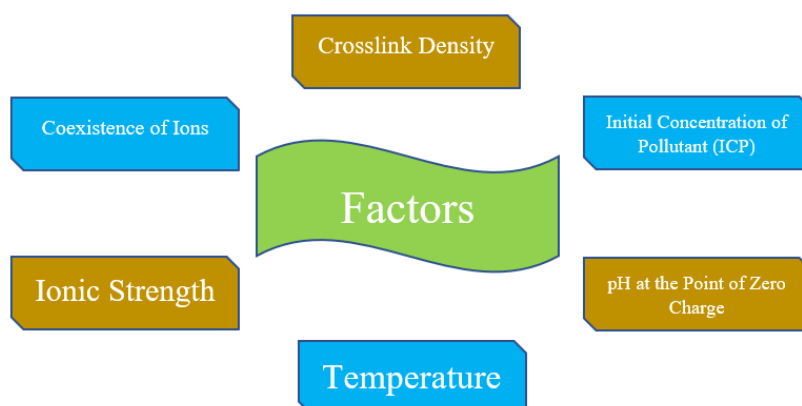


Fig. 2.6. Factors Affecting the Adsorption Capability of cellulose-based hydrogels

D. Temperature

The adsorption capacity of cellulose-based hydrogel rises as temperature goes up in the endothermic adsorption process, in contradiction to exothermic adsorption [100], [135]. The cellulose-based hydrogel's propensity to adsorb dyes from aqueous solutions normally increases in correlation to temperature [68], [80], [136]. At higher temperatures, dye molecules' mobility rise noticeably [68], offering a greater potential

to improve the interactions between dye molecules and the adsorbent surface. Consequently, there is less dye desorption from the surface of the adsorbent, raising the adsorption efficiency

E. Ionic Strength

Various salts and ions, such as calcium, magnesium, potassium, sodium, sulphate, and chloride, are present in industrial waste water along with other pollutants, and these salts have a major impact on the performance of cellulose-based hydrogels during the treatment of wastewater. When the swelling ability of CBHs was investigated based on ion valence, the biggest declination was discovered, in a decreasing sequence, with these trivalent cations present: trivalent, divalent, and monovalent. [51], [137].

F. Coexistence of Ions

Depending on whether an ion is positively or negatively charged, the presence of various ions in an aqueous solution influences the adsorption efficiency of hydrogel in numerous manners. In a solution with multiple ions, some of them may compete with others and reduce their adsorption, whereas others may co-adsorb with others to collectively increase adsorption [51], [79], [138]. An additional explanation for the low level of heavy metal adsorption can be the fact that the solution's ions already present share hydrogel binding sites [138], [139]. Additionally, based on an ion's properties like ionic diameter, electronegativity, and ionisation potential, functional groups encapsulated in hydrogel chains of polymers have shown preferred adsorption for a certain ion.

2.5.4. Constraints of Commercializing Hydrogel Technologies

It is well acknowledged that commercializing hydrogel primarily for use in wastewater treatment facilities has many benefits. Several areas of study still need to be explored in order to fully incorporate hydrogel engineering, including thorough testing for reliability targeted at mechanical characteristics, renewability, swelling ratio, heat resistance and pH sensitivity. [140]. The capacity to reuse modified hydrogel expands its range of applications, surpassing the limitations of regular hydrogel, which becomes brittle and loses rigidity with successive swelling [141]. Therefore, it is essential to increase hydrogel's ability to heal itself after swelling and boost its mechanical endurance [142].

2.5.5. Application of CBHs as Water Retaining Agent

One of agriculture's most important processes is irrigation, which helps plants and crops grow and develop by adding nutrients to the soil. Since they are cheaper and more effective in locations with little water resources, cellulose-based hydrogels have become a possible alternative to irrigation techniques. Together with the ongoing irrigation feature of this procedure, they lower the cost. Hydrogel aqueous solutions' substantial swelling and retention abilities help to maintain the soil's moisture content [77]. CBHs hydrogels are used in agriculture as they retain fertilisers in the soil, restrict the release of active compounds into groundwater, promote plant development, and consume less water and watering [78].

- CBHs hydrogel as water retaining agent

Due to HGs' excellent ability to absorb and hold water, they may preserve, keeping the soil moist. The soil is amended with the recommended number of cellulose-based hydrogel granules. After the soil has been watered, the granules absorb water and then gradually discharge it when the soil dries up. By doing this, agricultural water loss and losses caused by evaporation are avoided. As the HGs stretch and swell from absorbing and holding water, the soil gets more porous, improving the roots' access to oxygen. CBH's hydrogel was used as a conditioner for the soil in areas that are prone to drought to promote plant growth [97]. Porogen insertion increases porosity, which boosts root growth, seedling growth rates, and soil erosion resistance since less soil is compacted. The quantity of oxygen delivered to plant roots rises with greater porosity [73].

2.6. Conclusion

Heavy metals and dyes, which are released by a range of enterprises and have a detrimental effect on the environment, human wellness, and marine life, are two of the most common contaminants in wastewater. Therefore, for a more secure atmosphere, toxins from wastewater must be removed. The adsorption procedure, which is regarded to be an efficient and successful method to treat contaminated

water, uses many types of adsorbents. Nevertheless, the majority of treatment adsorbents are synthetic and non-disposable, making the handling of adsorbents a further environmental concern after treating wastewater. In order to find an adsorbent, researchers are seeking for materials that are naturally generated, sustainable, and recyclable. In this article, we reviewed the history, synthesis techniques, application, and current advancements in hydrogel synthesis based on cellulose. Outstanding adsorption and separation ability for various aqueous contaminants by HGs is systematically presented in this article. Because these HGs have the ability to store a large amount of water or biological fluids and release varying amounts based on their environment, they are ideal candidates for soil moisturisers used in urban agriculture. Thus, Cellulose-based hydrogels (CBHs) are excellent choices for wastewater treatment and water management in farming since they satisfy the criterion while also offering further advantages such as high removal effectiveness, high absorptivity, cost-effectiveness, and simplicity.

2.7. AIM AND SCOPE OF STUDY

- i. Synthesis of a Superabsorbent Hydrogel from Cellulose which is extracted from Agro-waste (Sugarcane bagasse).
- ii. Analysing the porous structure, absorptivity, and thermal stability of the cellulose-based hydrogel using characterization techniques.
- iii. Investigating the cellulose content in treated agro-waste (Sugarcane bagasse).

CHAPTER 3

EXPERIMENTAL SECTION

Details on the experimental procedures, the experimental protocol employed throughout the investigation, and the procurement of research supplies are included in this chapter. The numerous chemicals used, the extraction procedure, the pre-treatment technique, and the method for calculating the amount of cellulose in treated sugarcane bagasse are all covered in this chapter.

3.1. Materials and Cellulose Pre-treatment

3.1.1. Materials

Sugarcane bagasse was collected from local sugarcane juice shop, Delhi, India.

It was oven-dried after being sun-dried for 24 h at 100°C. The dried bagasse was powdered using grinder. All other chemicals sodium hydroxide (NaOH) and sulphuric acid (H₂SO₄) used for pre-treatment of sugarcane bagasse were taken. The substances involved had to be of the analytical grade.

3.1.2. Pre-treatment of Sugarcane Bagasse

Bagasse made from freshly cleaned sugarcane was cut into small pieces and allowed to dry outside for two days to lower the moisture level “fig. 3.1.”. The pieces were then dried for 24 hours at 100°C in an air dry oven. Using a grinder, sugarcane bagasse (UB, untreated bagasse) was reduced to powder “fig. 3.2.”. Pre-hydrolysis was performed on the sugarcane bagasse (1.0 g) using sulfuric acid (15 mL, 1.5% w/v) at 100°C for 3 hours. The pre-hydrolyzed material was pulped with sodium hydroxide (17.5%) at 100°C for 3 hours, and the pulp that resulted was filtered and washed with distilled water numerous times. It was air-dried at room temperature until the pH level hit 7, resulting in treated bagasse being richer with cellulose components. This proportion was referred to as treated bagasse (TB) “fig. 3.3.” & “fig. 3.4.”.



Fig. 3.1. Raw sugarcane bagasse



Fig. 3.2. Powdered sugarcane bagasse



Fig. 3.3. Untreated sugarcane bagasse

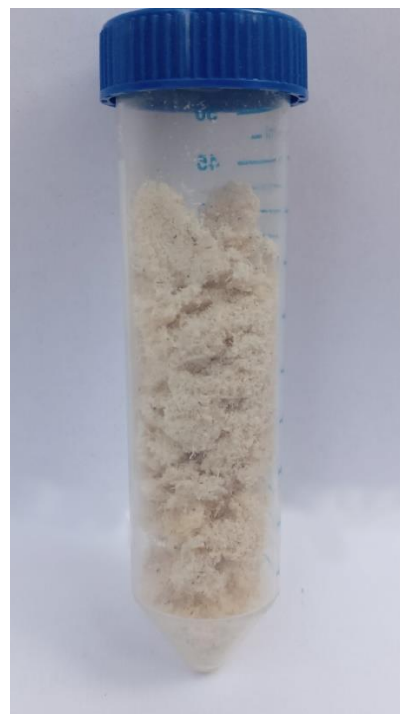


Fig. 3.4. Treated sugarcane bagasse

3.2 Estimation of cellulose content in treated bagasse

3.2.1 Principle

When treated with 67% H₂SO₄, acetylated cellodextrins, which are formed as a result of the acetolysis of cellulose with acetic/nitric reagent, dissolve and hydrolyze to produce glucose molecules. This glucose molecule is dehydrated to create hydroxymethyl furfural, which reacts with anthrone to produce a green product with a 630 nm colour intensity.

3.2.2 Materials

Sugarcane bagasse collected was pre-treated using above described procedure. This fraction of treated bagasse (TB) was is enriched with cellulose. The chemicals used for the estimation of cellulose content in TB are Acetic/Nitric Reagent (Mix 150ml of 80% acetic acid and 15mL of concentrated nitric acid), Anthrone reagent (Dissolve 200mg anthrone in 100mL of ice-cold 95% sulphuric acid), and 67% sulphuric acid. Prepare fresh and chill Anthrone reagent for 2h before use.

3.2.3 Estimation of Cellulose content in TB

A test tube containing a known quantity of the TB sample (1g) and 3 mL of acetic/nitric reagent was combined in a vortex before being heated in a water bath at 100°C for 30 minutes. The material is then centrifuged for 15 to 20 minutes after being cooled to room temperature. The leftover material was cleaned with MilliQ water after the supernatant was discarded. The sample was then treated with 10 mL of 67% sulfuric acid, which was then diluted from 1 mL to 100 mL after being left to stand for 1 hour. Later, a predetermined amount of anthrone reagent (10 mL of anthrone reagent to 1 mL of this diluted solution) was applied to the sample. The tubes are then heated for 10 minutes in a water bath, cooled, and the colour was determined at 630 nm. Using distilled water and anthrone reagent, a blank was created. After carrying out the aforementioned technique for 100 mg of cellulose, colour was generated using a succession of quantities (say, 0.4 to 2 mL equal to 40–200 mg of cellulose). The estimated cellulose content of pre-treated sample was 10 mg/g bagasse.

CHAPTER 4

CHARACTERIZATION TECHNIQUES

4.1. Thermogravimetric Analysis

TGA is an investigative technique for assessing a compound's thermal durability. The sample's loss of weight is calculated in this investigation as a function of temperature over a period of time. This approach also provides data on thermal breakdown, adsorption, desorption, and absorption.

The thermogravimetric analyzer, a device employed in TGA, is made up of a precision balance enclosed inside a combustion chamber and a specimen holder. In most cases, percentage of weight is monitored while the temperature is raised at a consistent pace. During the thermal reaction in TGA, which is carried out under an inert environment, particularly N₂ gas, the temperature often approaches 1000 °C. TGA also offers a curve between temperature and mass %. If the substance is thermally stable, there won't be any observable mass shift and there will be no slope in the TGA record. This method is also employed to gauge the polymers' heat stability.



Figure 2.3. Perkin Elmer Pyris diamond (TGA/DTA/DSC) system

4.2. Fourier transform infrared (FTIR) spectroscopy

This method is used to determine the identity of an unknown substance, the proportion of each component in a combination, and the functional group of an organic compound. The theory guiding infrared spectroscopy states that molecules have a tendency to absorb infrared area frequencies. Not all bonds inside a molecule absorb infrared light. Only those bonds are considered infrared active molecules because they exhibit a change in their dipole moment. The primary goal of infrared spectroscopy is to distinguish between the two chemicals in the fingerprint region (below 1500 cm^{-1}) under similar conditions.

Due to the molecules' bending and stretching vibrations, this fingerprint region has a significant number of absorption bands. Therefore, some compounds can be easily identified because they exhibit comparable absorption above 1500 cm^{-1} but differing absorption in the fingerprint area. Some of the infrared light is absorbed and some is transmitted when it passes through the sample. The resulting spectrum gives that sample a molecular fingerprint. Molecular rotation occurs as a result of the infrared radiation's absorption (less than 100 cm^{-1}), which causes discrete lines to emerge in the spectrum. Molecular vibration occurs when the sample is exposed to more intense radiation (10^4 to 10^2 cm^{-1}). In the infrared area, these quantized absorptions generate rotation and vibration. A molecule of an organic compound will exhibit an array of peaks in the infrared spectrum. The compound's structural details are sufficiently revealed by infrared spectroscopy.

Infrared spectroscopy is best performed using the Fourier transform. It is related to the interferometer, a basic optical instrument. As a result, a signal known as an interferogram is produced, which is then transformed into the necessary spectrum, which contains information about each molecule.



Figure 4.2. Perkin Elmer Two-Spectrum FTIR spectrometers

4.3. Scanning Electron Microscopy (SEM)

SEM is a powerful technique that provides data on the morphology, topography, and crystallographic information of a specimen. A two-dimensional picture of the substance is produced. Since this method relies on the electron beam, the sample should be dry before mounting and should be electrically conducted. In order to render non-coating material electrically conductible for imaging, a very thin layer of gold coating is applied via sputtering. These are the fundamental elements of SEM. The free electrons are created using a SEM thermionic emission gun, and a magnetic lens then transforms them into a fine beam. The sample is struck by this accelerated beam, and an image is created by rastering the beam. Different signal types, including secondary electrons, back-scattered electrons, auger electrons, and x-rays, are generated. These signals give details about the topography, atomic number, sensitivity, and composition of the surface, respectively. Only secondary electrons are picked up by the SEM, and this results in the creation of a picture that shows the sample's surface topography.



Figure 4.3. Scanning Electron Microscope (JEOL Japan Mode: JSM 6610LV)

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Thermogravimetric Analysis

Fig. 4.1. displays the results of the thermogravimetric analysis (TGA) for the treated SB and untreated SB. The degradation of the fibres started about 260°C, according to the two curves. Moisture evaporated during the phase from 40 to 150°C. The fibres broke down in two phases. The first phase involved the breakdown of cellulosic components like hemicellulose and cellulose (the range of temperatures of the degradation was from 190 to 400°C) [143]. The breakdown of non-cellulosic elements in the fibres caused the next stage of breakdown (400–469°C) [143]. The TGA data show that the acidic treatment had no effect on the thermal properties of the bagasse. It can be explained in terms of the amount of lignin, which serves as a powerful adhesive between the fibres, and the difficulty of acidic and alkaline solution penetration into these regions [144].

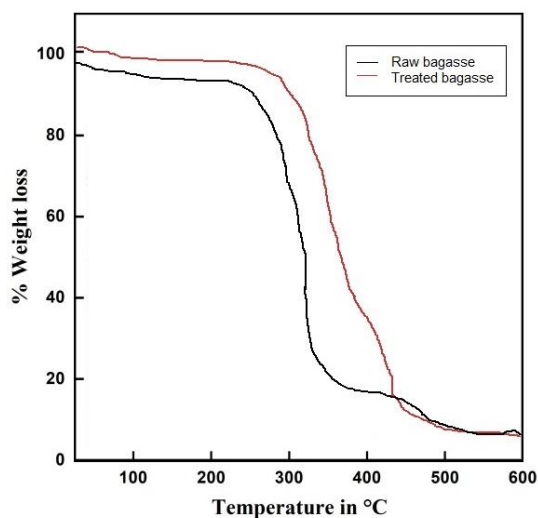


Fig. 5.1. TGA curves of the untreated and treated SB fibers

5.2. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra of the treated and untreated SB may show significant changes in terms of functional groups attached shown in fig. 4.2. and fig. 4.3. respectively. The bands of absorption in the 600 cm^{-1} to 4000 cm^{-1} region served as a representation of the molecules' functional group. In accordance to the spectrum, the functional groups of Si, O, and H were characterised by wavenumbers ranging from 600 cm^{-1} to 4000 cm^{-1} . The overall trends of the results were nearly identical, with the spectrum pattern being the only noticeable difference.

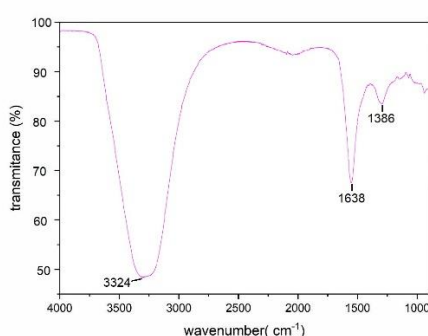


Fig. 5.2. FTIR spectra of treated SB

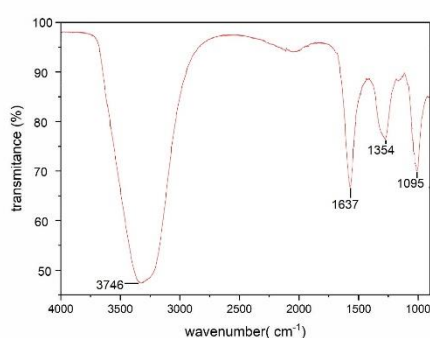


Fig. 5.3. FTIR spectra of untreated SB

The band spanning from 3500 to 3000 cm^{-1} was where the most noticeable changes were detected between the spectra of treated bagasse of sugarcane (NaOH-SB) at pH 7 and untreated original bagasse (Ori-SB) at pH 7. The wavenumber for the Si-O-Si stretching was exhibited at peak 968 cm^{-1} . Both spectra showed peaks at 3746 cm^{-1} (Ori-SB) and 3324 cm^{-1} (NaOH-SB), which stood for the peak for the -OH group that was present in the sample, respectively. While the existence of H-O-H/H₂O (adsorption of H₂O) was indicated by the peak seen between 1095 cm^{-1} and 1637 cm^{-1} .

5.3. Scanning Electron Microscopy (SEM) analysis

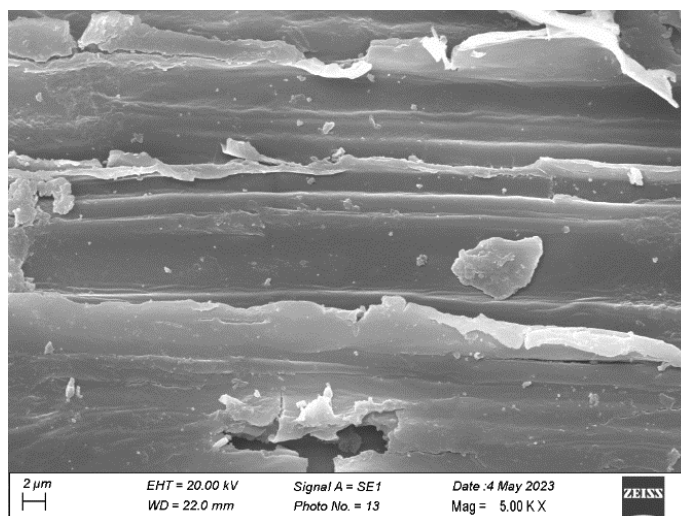


Fig.5.4. SEM image of Untreated Bagasse

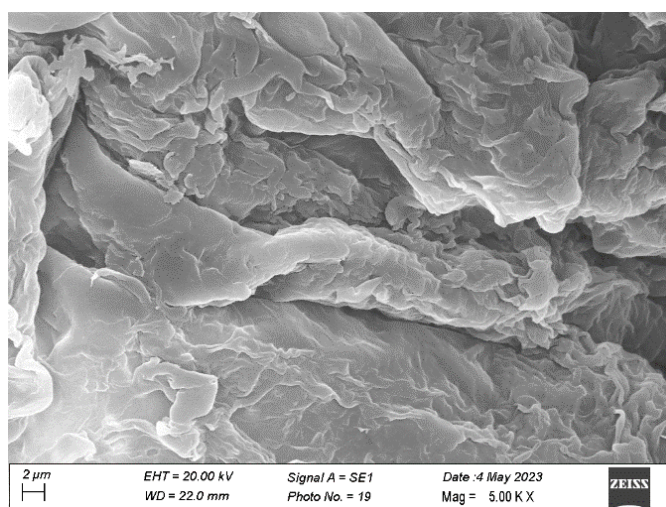


Fig.5.5. SEM image of Treated Bagasse

Fig.5.4. shows the SEM image of Untreated Bagasse which represents the smooth surface before acid treatment and Fig.5.5. shows the SEM image of Treated Bagasse represents the rough surface after acid treatment. The smooth surface is due the presence of oil and waxes on cell wall layer of sugarcane bagasse and after the acid treatment the cell wall layer get destroyed and rough surface of cellulose is visible.

CHAPTER 6

CONCLUSION

Based on the findings of the study, the following conclusions were drawn. According to TGA, the two curves indicate that fibre breakdown began about 260°C. Between 40 and 150°C, moisture evaporated during the phase. The fibres disintegrated in two stages. Cellulosic elements like hemicellulose and cellulose were broken down in the first phase (degradation temperatures ranged from 190 to 400°C). The following stage of breakdown (400-469°C) was brought on by the breakdown of non-cellulosic components in the fibres. The TGA measurements demonstrate that the acidic treatment had no impact on the bagasse's thermal characteristics. It can be explained by the presence of lignin, which acts as a strong glue between the fibres, and the difficulty of penetrating these areas with acidic and alkaline solutions. According to FTIR, the peak was moved from 1096 cm⁻¹ to 1638 cm⁻¹ showing the existence of water adsorption (H-O-H). Different peaks are for different components like cellulose, hemicellulose and lignin present in the bagasse. The FTIR results suggest a reduction in the hemicellulose and lignin content following acid-alkaline treatment of the fibers. The morphology of SB fibers was investigated using SEM to determine the change of fiber surface and morphology during extraction processing, showed the morphology of untreated and treated SB fibers, respectively. The surface of untreated SB fibers presented the smooth surface due to the presence of oil and waxes on cell wall layer which get destroyed after acid-alkali treatment and rough surface of cellulosic component get visible. The estimated cellulose content of the treated SB is 10 mg per gram of bagasse. These study helps to make effective cellulose based hydrogel from sugar bagasse.

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