APPLICATIONS OF CHITOSAN BASED MATERIALS IN WASTEWATER SYSTEMS

Abstract

Chitosan based materials (CBM) have emerged as a major area of study for both industry and academia. This chapter focuses on the classification of CBM based on the parameters such as physical modification used, chemical modification used, type of crosslinker used, type of initiator used and type of monomer used for the synthesis of the CBM with a focus on different types of method used for the synthesis of CBM and its applications in various domains. In addition to that, it also gives an overview of the synthesis procedure for different CBMs such as chitosan hydrogels, chitosan nanoparticles, chitosan sponges, chitosan beads, interpenetrating and semi-interpenetrating networks of CBM with focus on different characterization techniques to check different characteristics of the synthesized CBM for different applications.

Keywords: Chitosan based materials, chitosan hydrogels, chitosan beads, interpenetrating and semi-interpenetrating networks of CBM

Authors

Navneet Kaur Bhullar
Department of Chemical Engineering
University Institute of Engineering
Chandigarh University
Mohali, Punjab, India.

Devyanshu Sachdev
Dr. Shanti Swarup Bhatnagar
University Institute of
Chemical Engineering
& Technology
Panjab University
Chandigarh, India.

Kamlesh Kumari
Department of Chemical Engineering
Sant Longowal Institute
of Engineering & Technology (SLIET)
Longowal, Punjab, India.

I. INTRODUCTION

Chitin is the most abundant biopolymer in nature after cellulose and is the precursor to chitosan. It is present in a variety of eukaryotic species, including fungi, insects and crustacea [1]. The aminoglucopyrans chitin and chitosan are made up of glucosamine (GIcN) and acetylglucosamine (GlcNAc) residues. The potential uses of these renewable polysaccharides in the food, pharmaceutical, cosmetic, biomedical, biotechnological, agricultural and non-food sectors (such as water treatment, paper and textiles) are used owing to their exceptional biological activity, full biodegradability, outstanding biocompatibility and a little toxicity, these special polymers have become a new class of physiological materials with extremely complex functionalities [2]. Chitosan can be derived from different sources, including shrimp shells, crab shells, or fungal chitin, and the source can impact the properties of the material. Chitosan possesses several unique properties that make it valuable for a wide range of applications in various fields, including medicine, agriculture, the food industry, and wastewater treatment. Some of the notable properties of chitosan include biodegradability, biocompatibility, non-toxicity, antibacterial properties, and its ability to form films and gels.

1. **Chitosan Derivatives:** In addition to chitosan, several derivatives have been synthesized by chemically modifying its structure to enhance specific properties or tailor it for particular applications. Some common chitosan derivatives include:

    - **N-acylated Chitosan:** Acylation of chitosan can improve its solubility and film-forming properties.
    - **O-carboxymethyl Chitosan:** This derivative has improved water solubility, making it suitable for biomedical and pharmaceutical applications.
    - **Quaternized Chitosan:** Quaternization introduces permanent positive charges, enhancing the antimicrobial properties of chitosan.
    - **Chitosan Nanoparticles:** Chitosan nanoparticles are prepared by reducing chitosan to nanoscale dimensions, which increases its surface area and makes it useful for drug delivery and wastewater treatment applications[3,4].
    - **Chitosan Oligosaccharides**: Chitosan can be enzymatically or chemically hydrolyzed into smaller oligosaccharides, which exhibit enhanced biological activities, such as antioxidant and immunostimulatory effects[5]. These chitosan derivatives offer tailored functionalities and expanded applications compared to native chitosan. The versatility of chitosan and its derivatives has led to significant research and development efforts aimed at exploring their potential in various industries and environmental applications considered to ensure their safe and sustainable use in pollutant removal processes.

2. **Classification of Chitosan-based Materials:** CBM can be classified into various categories based on their properties, modifications and applications. Chitosan is a biopolymer derived from chitin, and it has a wide range of uses in different fields due to its biocompatibility, biodegradability, and versatile characteristics. **Table 1** depicts the physical and chemical modifications of CBM whereas **Table 2** depicts the cross-linker used, monomer used and initiator used for CBM. The CBM can be classified based on physical modifications, chemical modifications, crosslinker used, monomer used and initiator used. Physical modification is a straightforward method that doesn’t need a

catalyst or the finished product to be purified. Chemical modifications help in tailoring different characteristics such as solubility, charge density and reactivity. Crosslinkers play a crucial role in stabilizing CBM and tailoring their properties for specific applications in areas like drug delivery, tissue engineering and biotechnology. Initiators are often used in processes involving polymerization, grafting or other chemical reactions which also serve as catalysts in various reactions involving chitosan enabling the synthesis of CBM with tailored properties for a wide range of applications including drug delivery, tissue engineering and coatings. Monomers are generally used to modify CBM which are chosen based on their reactivity, and desired functional groups, allowing for the customization of CBM for specific applications in areas such as biomedicine, environmental remediation and coatings.

Table 1: Physical and Chemical Modification of the CBM

Type of modification	Description	Purpose/Applications
Physical modifications		
Crosslinking	Introduction of chemical crosslinks between chitosan chains or with other polymers.	Enhanced stability, mechanical strength, and controlled release in drug delivery systems, tissue engineering, and wound dressings.
Freeze-Drying	Removal of water under low temperature and reduced pressure conditions.	Formation of porous chitosan structures like sponges and aerogels for wound dressings, drug delivery, and tissue scaffolds.
Solvent Casting	Chitosan solution is cast into a mold, and the solvent is allowed to evaporate.	Creation of chitosan films with controlled thickness and mechanical properties for various applications, including coatings.
Electrospinning	Electrostatic force is used to form chitosan nanofibers from a polymer solution.	Fabrication of nanofiber mats for tissue engineering, wound dressings, and drug delivery systems.
Spray-Drying	Atomization of chitosan solution followed by rapid drying using hot air.	Production of chitosan microspheres or nanoparticles for controlled drug release and encapsulation.
Ionic Gelation	Crosslinking of chitosan with oppositely charged ions (e.g., tripolyphosphate).	Formation of chitosan nanoparticles or microparticles for drug delivery and encapsulation purposes.
Coating/Immersion	Coating or immersing substrates in chitosan solution to deposit a chitosan layer.	Surface modification for applications like wound dressings, drug delivery systems, and antimicrobial coatings.
Compression Molding	Chitosan is compressed into desired shapes under heat and pressure.	Manufacturing of chitosan-based products with specific shapes, such as tablets and implants.

Phase Inversion	Chitosan is dissolved in a solvent and then precipitated by changing the solvent or temperature.	Preparation of chitosan membranes with controlled porosity for filtration and separation applications.
Ultrasonication	Application of high-frequency sound waves to disperse or homogenize chitosan solutions.	Improved dispersion of chitosan in solutions, enhancing its stability and uniformity in various applications.
Lyophilization (Freeze Drying)	Chitosan materials are frozen and then dried under a vacuum.	Creation of porous structures and improved stability of chitosan materials, including sponges and aerogels.
Microwave Processing	Exposure of chitosan materials to microwave radiation for drying or modification.	Rapid drying and sterilization of chitosan materials for medical and food applications.
Heat Treatment	Chitosan materials are subjected to controlled heating.	Alteration of chitosan properties, such as crystallinity, to achieve desired characteristics for specific applications.
Chemical Modifications		
Acetylation	Introduction of acetyl groups (-COCH3) to chitosan, increasing its solubility in organic solvents.	Enhanced solubility for use in drug delivery systems, film formation, and wound dressings.
Carboxymethylation	Carboxymethyl groups (-COOCH3) are added to chitosan, improving its water solubility and swelling properties.	Creation of water-soluble chitosan derivatives for drug delivery, biotechnology, and food applications.
Quaternization	Introduction of quaternary ammonium groups (e.g., -NR4+) to chitosan, resulting in positively charged derivatives.	Antimicrobial materials, flocculants, and gene delivery vectors with enhanced binding properties.
Thiolation	Addition of thiol (-SH) groups to chitosan, improving its interaction with metals and other thiol-reactive compounds.	Development of CBM for heavy metal removal and controlled drug release.
Amidation	Chitosan is reacted with acylating agents to introduce amide (-CONH2) groups, enhancing its stability and functionality.	Improved mechanical properties and resistance to enzymatic degradation in various applications.

Graft Copolymerization	Polymer chains are grafted onto the chitosan backbone via chemical reactions.	Tailoring chitosan properties for specific applications, such as drug delivery and tissue engineering.
Schiff's Base Formation	Reaction of chitosan with aldehydes to form Schiff's base linkages (-CH=N-) that can be further modified.	Functionalization of chitosan for drug delivery, wound healing, and tissue engineering.
Click Chemistry	Utilization of click reactions (e.g., azide-alkyne Huisgen cycloaddition) to attach functional groups to chitosan.	Precise modification of chitosan for a wide range of applications, including bioconjugation.
Sulfonation	Sulfonic acid groups (-SO3H) are introduced to chitosan, improving its cation exchange capacity.	Creation of chitosan derivatives with enhanced ion exchange properties for adsorption and catalysis.
Esterification	Reaction with organic acids or acid chlorides to form ester bonds (-COO-) with chitosan.	Enhanced film formation, stability, and hydrophobicity for coatings and encapsulation.
Nitration	Nitro groups (-NO2) are introduced to chitosan through nitration reactions.	Formation of CBM with specific chemical properties, such as increased electron density.
Photo crosslinking	Chitosan is functionalized with photoreactive groups, enabling crosslinking under UV or visible light.	Development of photo-responsive chitosan materials for drug delivery and tissue engineering.

Table 2: Classification of CBM based on usage of Crosslinker, Monomer and Initiator

Type of crosslinker used		
Crosslinker	**Description**	**Purpose/Applications**
Glutaraldehyde	A bifunctional crosslinker with aldehyde groups that react with chitosan amino groups.	Crosslinking chitosan for the formation of hydrogels, beads and membranes.
Tripolyphosphate (TPP)	An ionic crosslinker that reacts with chitosan to form insoluble nanoparticles or microspheres	Formation of chitosan nanoparticles for drug delivery systems and encapsulation.
Genipin	A natural crosslinker extracted from gardenia fruit that forms stable crosslinks with chitosan.	Enhancing the stability and biocompatibility of CBM

Sodium Sulphate	An ionic crosslinker is used in conjunction with other reagents to cross-link chitosan.	Application-dependent crosslinking of CBM
Sodium tripolyphosphate	Another form of tripolyphosphate is used as a crosslinker in CBM formulations.	Formation of chitosan nanoparticles for drug delivery and food applications.
Citric acid	A non-toxic crosslinker that forms ester bonds with chitosan hydroxyl groups.	Crosslinking chitosan for various biomedical and food applications
Epoxy compounds (eg: DGEBA)	Epoxy-based crosslinkers that react with chitosan amino groups	Modification of chitosan for tissue engineering and drug delivery.
Polyethylene glycol diglycidyl ether (PEGDGE)	PEG-based crosslinker that reacts with chitosan amino groups	Creating biocompatible chitosan hydrogels for biomedical applications
Ethylene glycol dimethacrylate (EGDMA)	Methacrylate-based crosslinker that forms covalent bonds with chitosan	Preparation of chitosan-based polymer with enhanced mechanical properties
1,4-butanediol diglycidyl ether (BDDE)	An epoxy-based crosslinker used in chitosan modification	Development of crosslinked chitosan for controlled drug delivery
Type of Initiator Used		
Ammonium persulphate (APS)	A chemical initiator that generates free radicals for polymerization reactions	Initiation of graft copolymerization reactions with chitosan for modified material properties
Potassium persulphate (KPS)	KPS is used as an initiator for free radical polymerization reactions.	Polymerization of chitosan with other monomers or polymers for tailored properties.
2,2'-Azobis(2-methylpropionitrile) (AIBN)	A thermal initiator that decomposes to produce radicals at elevated temperatures	Initiation of thermal polymerization reactions involving chitosan and other compounds
Benzoyl peroxide (BPO)	A chemical initiator commonly used in polymerization reactions at moderate temperatures	Polymerization and crosslinking reaction involving chitosan and acrylic or methacrylic monomers.
Hydrogen Peroxide (H_2O_2)	A mild oxidizing agent that can initiate grafting reactions with chitosan	Grafting of functional groups or polymers onto chitosan for improved properties
UV photoinitiators (eg: photoinitiator Irgacure 2959)	Initiators that initiate polymerization reactions when exposed to UV light	Photopolymerization of chitosan based hydrogels and coatings for biomedical

		applications.
Redox Initiators (eg: APS/sodium metabisulphite)	Combines a reducing agent with APS to initiate polymerization reactions	Initiation of redox polymerization reaction involving chitosan and other compounds
Thermal Initiators (eg: Azo initiators)	Initiators that initiate polymerization reactions when heated to specific temperatures	Thermally-induced polymerization of chitosan and compatible monomers.
Type of monomer used		
Acrylic acid (AA)	A carboxylic acid monomer that introduces carboxyl groups into chitosan	Graft polymerization with chitosan to enhance water absorption and drug loading capacity.
Methacrylic acid (MAA)	A methacrylate based monomer used for grafting onto chitosan to modify its properties	Preparation of chitosan based hydrogels and membranes for drug delivery and wound healing
N-vinyl pyrrolidone (NVP)	A hydrophilic monomer that improves the water-absorbing capacity of chitosan	Formation of chitosan based hydrogels for controlled drug release and tissue engineering.
Styrene	An aromatic monomer that can be copolymerized with chitosan to create hybrid materials	Modification of chitosan for applications in adsorption, separation and coatings
2-Hydroxymethyl methacrylate (HEMA)	A hydrophilic methacrylate monomer used for the preparation of chitosan hydrogels	Development of chitosan-based hydrogels for drug delivery, tissue engineering and wound dressing.
Glycidyl Methacrylate (GMA)	A monomer with epoxy groups that can be used for chitosan modification	Introduction of functional epoxy groups onto chitosan for further reactions.
Itaconic Acid	A dicarboxylic acid monomer that can be grafted onto chitosan to introduce carboxyl groups	Formation of chitosan derivatives for applications in drug delivery and tissue engineering
Allyl Glycidyl Ether	This monomer is used for chemical modification of chitosan	Creation of chitosan derivatives with allyl groups for further reactions
2-Acrylamido-2-methylpropane Sulfonic Acid (AMPS)	An anionic monomer used for grafting onto chitosan to enhance its ion exchange capacity	Development of CBM for adsorption and wastewater treatment
1-Vinyl-2-pyrrolidinone (VP)	A hydrophilic monomer used for copolymerization with chitosan to improve water absorption	Preparation of chitosan based hydrogels for drug delivery systems and wound healing.

3. **Different methods used for the preparation of Synthesized Chitosan Based Materials:** The preparation of CBM which is synthesized by the introduction of different materials in combination with chitosan for tailoring different characteristics of the synthesized materials for different materials. The different methods with descriptions and their applications are depicted using **Table 3**.

Table 3: Different methods with description and applications of synthesized CBM

Method	Description	Applications	Ref.
Solution Mixing or Blending	Chitosan and other materials are mixed in solutions	Film coatings and composites	[6]
In-situ synthesis	Different materials are synthesized within the chitosan matrix	Drug delivery, catalyst and sensors	[7]
Sol Gel method	Formation of a gel like solution where chitosan and other materials react.	Silica chitosan hybrids and encapsulation	[8]
Emulsion method	Dispersion of one material in droplets within another material	Chitosan nanoparticles and drug delivery systems	[9]
Layer by layer (LBL) assembly	Deposition of layers of CBM	Multilayer thin films and coatings	[10]
Electrospinning	Development of nanofibers or nanofibers mats from different materials	Tissue scaffolds and wound dressings	[11,12]
Co-precipitation	Hybrid materials are precipitated from a solution	Nanocomposites with nanoparticles	[13,14]
Hydrothermal method	Mixing of different materials with chitosan under high pressure and high temperature conditions.	Hydrogels and ceramics	[15,16]
Green synthesis	Using eco-friendly approaches with natural extracts or biocompatible reducing agents	Eco-friendly drug delivery	[17,18]
Spray drying	Spray solution containing chitosan and other materials into a hot chamber	Particle encapsulation and drug delivery systems	[19]
Template assisted synthesis	Using different template materials with chitosan to create ordered structures of chitosan and other materials	Porous materials and membranes	[20]
Melt mixing	Development of hybrid material using melting, mixing and followed by cooling	Thermoplastic composites and films.	[21]

4. **Different analytical techniques for investigating different characteristics of chitosan based materials:** The assessment of synthesized CBM helps in evaluating the performance of different applications based on their structural, chemical, thermal, rheological, antibacterial, biological and mechanical characteristics. The summary of different studies in depicted using **Table 4.**

Table 4: Overview of different analytical techniques for CBM

Analytical Technique	Description	Purpose and application	Ref.
Fourier Transform Infrared (FT-IR) Spectroscopy	Determination of chemical bonds and functional groups in materials.	Identification of chitosan modification and final composition of CBM	[22]
X-ray diffraction (XRD)	Determination of crystal structure and crystallinity of materials	Investigation of the crystalline nature of chitosan and purity of the CBM	[23]
Scanning Electron Microscopy (SEM)	Determination of morphology of the material surface of different materials	Visualizing the morphology and structure of CBM for better understanding of the materials	[24]
Transmission Electron Microscopy (TEM)	Delivers the details of the morphology of nanoparticles and nanoscale structures.	Determination of the size and morphology of the CBM at nanoscale.	[25]
Atomic Force Microscopy (AFM)	Measurement of surface topology and mechanical characteristics at the nanoscale	Assessment of surface topology of CBM at nanoscale	[26]
X-Ray Photoelectron Spectroscopy(XPS)	Determination of electronic state and chemical composition of materials	Assessment of chemical composition and electronic state in different CBM	[27]
Nuclear Magnetic Resonance (NMR)	Determination of the molecular structure of the different materials	Determination of the chemical structure of chitosan and its derivatives.	[28]
UV-Visible Spectrophotometer	Determination of absorbance and different optical properties of the materials	Determination of adsorption capacity for dye and metal removal for CBM	[29]
Thermogravimetric analysis (TGA)	Determines the thermal stability of the materials by studying the change in the mass of materials w.r.t. temperature.	Determination of thermal stability, thermal degradation and inflection point for CBM.	[22]
Differential Scanning Calorimetry (DSC)	Determination of heat flow during phase transition, glass transition	Determination of different thermal characteristics for CBM in different heating and cooling	[30]

	temperature and crystallinity of materials	cycles.	
Dynamic mechanical analyzer (DMA)	Determination of material's viscoelastic properties and mechanical behavior	Assessment of mechanical characteristics for CBM	[31]
Zeta Potential Analyzer	Determination of surface charge of colloidal particles	Assessment of surface charge and colloidal stability of chitosan nanoparticles.	[32]
Particle Size Analyzer	Determination of particle size distribution of suspension	Assessment of size distribution of CBM	[33]
BET Surface Analyzer	Measurement of specific surface area of materials	Determination of surface area for adsorption studies	[34]
Contact Angle Measurements	Assessment of wettability and surface hydrophobicity or hydrophilicity	Measurement of super hydrophobicity of CBM	[35]
Rheological Analysis (Rheometer)	Measurement of flow and viscoelastic characteristics of materials	Determination of flow and viscoelastic characteristics of CBM such as gels and solutions	[36]
Gel Permeation Chromatography (GPC)	Determination of molecular weight and molecular weight distribution in materials	Determination of molecular weight distribution for CBM	[37]
High-Performance Liquid Chromatography (HPLC)	Determination of content in materials	Assessment of content and release of drugs from chitosan carriers	[38]
Biological and Biocompatibility Assessment	Determination of cell viability assays, cell adhesion and proliferation and in vivo studies	Assessment of cytotoxicity, biocompatibility, cell behavior, and tissue response in animal models for CBM	[39]

5. **Generalized process for Synthesizing Chitosan based Materials Method of Production of Chitosan-Based Material:** The synthesis of CBM involves several steps which comprise of extraction of chitosan from its natural sources to the development of different materials for a wide range of applications. The generalized form of synthesis is given in steps below:

    - **Chitosan Extraction:** Chitosan is typically extracted from natural sources, such as shrimp shells, Ganoderma Lucidum mushroom, Metapenaeus stebbingi shells and Crayfish Procambarus [40–43]. The extraction process of chitosan generally involves cleaning: shells are cleaned to eradicate impurities like protein and minerals, demineralization: shells are treated with acid to remove minerals, deproteinization:

enzymes or alkalis are used for removal of protein leaving chitin and deacetylation: chitin is treated with an alkali to deacetylate it and convert it into chitosan [44,45].

- **Chitosan Purification:** The chitosan obtained from the extraction process may be further purified to remove any remaining impurities, resulting in a higher-quality chitosan product.
- **Chitosan solution preparation:** Chitosan is often dissolved in an appropriate solvent to create a chitosan solution of the desired concentration in which different types of solvents are used such as acetic acid, hydrochloric acid and formic acid.
- **Material formulation:** The material formulation depends upon the intended application which can be further processed into different forms including chitosan films [46], chitosan nanoparticles [47], chitosan hydrogels [48], chitosan sponges [49,50]and chitosan beads [51,52]. The tailoring of different characteristics might lead to different modifications such as acetylation, cross-linking, grafting or functionalization with specific molecules using different types of agents which is further used for the stability and mechanical properties of CBM. Additional processing such as drying, sterilization or shaping into specific forms may be required depending upon the intent of the applications.
- **Characterization:** The synthesized materials are characterized for investigating different type of characteristics such as chemical, structural, morphological, rheological, thermal, mechanical biological and biocompatibility assessment using different analytical techniques. The detailed discussion of characterization is discussed in **Section 1.4** of this chapter.

6. **Different types of Chitosan Nanoparticles:** Chitosan nanoparticles can be prepared through various methods, resulting in different types of nanoparticles with unique characteristics. Some of the common types of chitosan nanoparticles include:

    - **Chitosan Nanoparticles (CSNPs):** These are the basic chitosan nanoparticles formed by the process of nanoprecipitation or ionic gelation. They have a spherical or quasi-spherical shape and can be used for various applications, such as drug delivery, gene delivery, and pollutant removal.
    - **Chitosan-Coated Nanoparticles:** Chitosan can be used to coat the surfaces of other nanoparticles, such as metallic nanoparticles (e.g., iron oxide nanoparticles) or inorganic nanoparticles (e.g., silica nanoparticles)[53,54]. The chitosan coating imparts stability, biocompatibility, and additional functionalities to the core nanoparticles.
    - **Chitosan-Modified Nanoparticles:** Chitosan can be chemically modified to introduce specific functional groups, such as quaternary ammonium, thiol, or carboxyl groups, which can enhance its interactions with pollutants, target-specific delivery, or tailor its properties for different applications.
    - **Crosslinked Chitosan Nanoparticles:** Chitosan nanoparticles can be crosslinked using various crosslinking agents to improve their stability and control the release of loaded substances[55,56] (e.g., drugs or antimicrobial agents). Crosslinked chitosan nanoparticles find applications in drug delivery and wound healing.
    - **Chitosan-Metal Nanoparticle Composites:** Chitosan can act as a stabilizing agent for metallic nanoparticles, such as copper, silver or gold nanoparticles, resulting in chitosan-metal nanoparticle composites[57]. These composites may have combined properties, such as antimicrobial activity and catalytic capabilities.

- **Chitosan-Grafted Nanoparticles:** Chitosan can be grafted onto the surface of other nanoparticles, such as carbon nanotubes or graphene oxide, to improve their dispersibility and biocompatibility[58]. These chitosan-grafted nanoparticles have potential applications in drug delivery and tissue engineering.
- **Chitosan-Magnetic Nanoparticles**: Chitosan can be combined with magnetic nanoparticles, such as iron oxide nanoparticles, to form chitosan-magnetic nanoparticle composites[59]. These composites can be easily separated from the solution using an external magnetic field, making them useful in wastewater treatment and drug delivery[60].

  Each type of chitosan nanoparticle has specific advantages and applications, depending on its properties and preparation method. The choice of chitosan nanoparticle type will depend on the intended application and the desired functionalities required for the particular use case. Researchers continue to explore novel synthesis methods and modifications to optimize chitosan nanoparticles for various biomedical, environmental, and industrial applications.

7. **Different types of chitosan based materials:** The CBM refers to a class of adaptable material developed from chitosan, a biopolymer composed of chitin, which is present in the shells of crustaceans. These materials are utilized in several industries and have drawn a lot of interest. The key information on materials based on chitosan is given as follows:

   - **Chitosan Hydrogels:** Chitosan hydrogels are networks of hydrophilic polymers that exhibit both liquid and solid characteristics that might expand in water without dissolving [61]. The hydrogel's water still has some action even though it is confined within the gel network. In addition to having a soft, rubbery quality typically similar to live tissues the completely expanded hydrogels have certain characteristics of living beings such as greater permeability to smaller molecules and the regulated release of imprisoned molecules [61]. Furthermore, a wide range of hydrogels was developed including membranes, sheets, solid molded forms, microparticles and coating [62]. Hydrogels are likewise scalable, ranging in size from nanometers to micrometers with their relative deformability allows them to easily take on the shape of an enlosed region. These characteristics have made it possible to use hydrogels in a variety of industries including industrial, agricultural, biomedical and medicinal. The researchers from China developed a highly effective and flexible polymeric network of hydrogel which was functionalized using semiconductive in-situ polymerization of MnO_2 NWs-chitosan structure which has application in solar driven steam generation [63]. The investigation showed that the governance of non-radiative relaxation phenomena for generation of thermal energy to heat pumping water into the vapour phase through the interstitial defects or oxygen vacancy which is revealed through the defect chemistry of the SPM-CH hydrogels and in addition to that the energy confined at liquid -gas interface synchronizes the tuning of hydrogen bonding from a bound state to an unbound water state which results in the generation of a maximum amount of intermediate water clusters with a lower vaporization enthalpy [63]. SPM-CH also showed excellent results in different characteristics such as compressive strain, solar absorption, smooth evaporation rate and outstanding conversion efficiency of solar to thermal energy under solar irradiance [63]. European researchers developed antifouling implant coatings in which brushes of polymer were functionalized using chitosan hydrogels for application in implanted biosensing devices that have better

tissue integration [64]. The functionalized technique, based on photoinduced SET-LRP and necessitating a low catalyst loading and mild conditions, is predicted by the method's use of easily accessible monomers and base coating materials found in current medical goods [64]. In addition to that, these antifouling polymer brushes demonstrated improved hemocompatibility by preventing blood cell components from adhering to and activating these coatings[64]. The scientists from France investigated the multi-membrane chitosan hydrogels as chondrocytic cell bioreactors in which the investigation on the biological behavior of chondrocytes within MMHs was observed and which was developed from physical hydrogels without the need for an external cross-linking agent and in addition to that it was also observed that the chondrocytes housed in a membrane-bound heparinized hydrogel (MMH) spontaneously aggregated, multiplied, preserved their phenotypic and generated a significant amount of cartilage type matrix proteins that filled the inter membrane space of the system [65]. After 45 days in culture, no signs of inflammation were seen and these multi-compartment bioreactors are intriguing because of their intricate chemical and physical architectures, which mimic more sophisticated biological media decays [65]. The researchers from India and Japan collaborated to investigate the chitosan hydrogel-hydroxyapatite composite developed using wet chemical synthesis for application in tissue engineering in which it was demonstrated that Hap deposition happened quickly or in less than 20 hours, on the surface of chitosan hydrogel membranes and in addition to that promising outcomes of excellent biocompatibility suggests that these membranes might find use in the field of tissue engineering [66]. The Iranian scientist developed a potent wound dressing material by integration of Saqez essential oil into a hybrid of polyvinyl alcohol/chitosan bilayer hydrogel in which investigation showed promising results with acceptable water swelling, water vapour transfer rate, mechanical and physical characteristics [67]. These bilayer hydrogels are a promising option for wound dressing since they have strong cell compatibility, appropriate blood compatibility and hemostatic potential and in addition to that they also showed a promising substitute for conventional products and have the potential to be a widely used antibacterial and antioxidant wound dressing [67]. The team of Brazilian researchers investigated the the sorption studies for cadmium metal and methylene blue dye using chitosan based hydrogel and hydrogel composite of chitosan-magnetite. The fitting into isotherm models showed that there are monolayer and multi-site interactions in the hydrogel network which also showed the maximum sorption capacities around 23 mg/g for methylene blue dye whereas the maximum sorption capacities for Cadmium removal for chitosan hydrogel and composite hydrogel was 90.038 and 80.383 mg/g respectively. In addition to that, the FTIR and TGA studies helped in confirming the interaction between the metal and dye with both hydrogels [68]. The Japanese researchers investigated the DNA-chitosan hydrogels for application in the adsorptive removal of pharmaceutical, organic dyes and different heavy metals which was well fitted into the pseudo-second-order kinetic model and the adsorbent shows the good adsorption capacity for different types of pollutants [69].

- **Chitosan Nanoparticles:** Chitosan nanoparticles possess both the chitosan and nanoparticles attributes, including small size and quantum size effects, surface and interface effects and small size [47]. Initially, these particles were prepared by emulsifying and crosslinking for intravenous delivery of anti-cancer drug 5-fluorouracil [47]. There are numerous methods such as ionotropic gelation,

microemulsion, emulsification solvent diffusion, polyelectrolyte complex and reverse micellar method for the synthesis of chitosan nanoparticles [47]. Out of these, the most widely used methods are ionotropic gelation and polyelectrolyte complex. These methods are simple and do not apply high-shear force or use organic solvents. The researchers from China investigated the nano-bio adsorbent made up of magnetic chitosan which was used for the removal of Cu (II) from the aqueous solution in which super magnetic property was investigated for particle size range from 8 to 40 nm [70]. The maximum adsorption of Cu (II) was more than 90% and a sorption capacity of 35.5 mg/g from Langmuir isotherm was calculated [70]. The scientists from Taiwan investigated magnetic chitosan nanoparticles characteristics for adsorption of Co (II) from the aqueous solution at a pH range of 3-7 and in addition to that it has a maximum adsorption capacity of 27.42 mg/g and shows an exothermic nature of the adsorption [71]. The Chinese researchers worked on the ethylenediamine modified by magnetic chitosan nanoparticles which was used for adsorption of acid dyes and maximum adsorption results were obtained at pH 4 and pH 3 for AO7 and AO10 respectively [72]. The results were also well fitted into the adsorption isotherm model and thermodynamic model which shows the spontaneous and exothermic nature of the adsorption [72].

- **Chitosan sponges:** Chitosan sponges are porous, 3-D structures that are often used in applications such as wound dressings, tissue engineering and drug delivery due to their biocompatibility and ability to absorb and release fluids. The researchers from the United Kingdom investigated the drug release and mechanical characteristics of alginate-chitosan sponge which depends upon the composition of the materials in which it was observed resistance to compression was maximum for chitosan alone in comparison to its counterparts whereas the resistance to breakage was lower for hybrid component systems [73]. The dissolution studies indicated a delayed release behavior for all systems apart from the alginate alone system [73]. The researchers from China worked on the skin tissue engineering material prepared from a gelatin-chitosan sponge scaffold in which impact of the ratio of chitosan and gelatin on different characteristics such as morphology, pore size, water uptake capacity, porosity, degradation behavior and water retention capacity [74]. The results indicate that the sponge had a homogeneous porous structure with pore size ranging from 120-140 μm, high porosity (>90%), high capacity for absorbing water (>1500%), high capacity for retaining water (>400%) and a degradation percentage from 38.3 to 53.9% in 28 days [74]. The antibacterial and hemostatic characteristics for accelerating wound repair by double crosslinking of chitosan sponge which majorly comprises of chitosan, graphene oxide and tannic oxide through simple crosslinking and alkaline gas treatment in which there was an enhancement in the mechanical test, solubility test and promoted the repair of wound in the rat full thickness model [75]. The investigators from Germany worked on the sustained release drug carrier by chitosan sponges in which it was observed that the crosslinking and drug release were pH dependent and in addition to that the release of the drug was controlled by changing the concentration of the drug, acetylation and crosslinking and corresponding to that it also followed the Higuchi's mechanism [76]. The Chinese investigators worked on the role of composite promoting wound healing which was made up of hydroxybutyl chitosan sponge which showed enhanced water absorption, porosity, softness and lower blood clotting index which might be due to the hydrophilic nature which further increases the blood concentration and viscosity that

lead to semi-swelling viscous colloid to clog capillaries [77]. In vivo tests on Sprague Dawley rats eventually demonstrated that epithelial cells adhered to the composite sponge and infiltrated its interior. Furthermore, it demonstrated that composite sponge (HC-1) was more effective in promoting wound healing and aided in the quicker formation of skin glands and re-epithelialization [77]. The anionic dye removal was carried out using hydrophobically tailored chitosan sponge preparation in which methyl orange was used as a model dye and it showed an adsorption capacity of 110 mg/g which showed best fitting into Langmuir and pseudo-second order and which better adsorption might be due to hydrophobic interaction and electrostatic attraction [78]. The Chinese researchers investigated graphene oxide and chitosan sponge composite which was used as a filter medium for the removal of methylene blue dye and the findings showed that the maximum adsorption capacity of 275.5 mg/g for the dye was observed for the 9% chitosan sponge content which carried out adsorption process through combination of hydrophobic interaction and electrostatic attraction [79].

- **Chitosan beads:** Chitosan beads are spherical particles made up of chitosan and they have a variety of applications including drug delivery, adsorption and enzyme immobilization. The Chinese scientists investigated the adsorption of cadmium and phosphate from aqueous solutions through lanthanum-iron incorporated chitosan beads which showed the adsorption capacity of 52 mg/g and 35.5 mg/g for phosphate and cadmium at a pH 6.5 respectively [80]. In addition to that, these beads showed excellent stability and reusability of 78.5% and 85.1% for phosphate and cadmium after four cycles respectively [80]. The investigators from Greece studied the adsorption characteristics of chitosan and β-cyclodextrin/chitosan beads against indigo carmine dye in which maximum adsorption capacity of 500 and 1000 mg/g respectively and in addition to that it followed the pseudo-second order kinetic model and adsorption process is spontaneous and exothermic which derived from the calculated thermodynamic parameters [81]. The Chinese researchers worked on the development of a drug delivery system based on materials porous starch, chitosan and pectin for a colon-targeted drug in which 86.20% of the loaded doxorubicin could reach the colon [82]. Furthermore, in vitro method of simulating digestion showed the effectiveness of delivery design was, since the upper gastrointestinal tract only released doxorubicin at a rate of 13.8%, while pecti/porous starch/doxorubicin and pectin/doxorubicin beads released the drug at 17.56 % and 67.04% respectively [82]**.**

- **Interpenetrating and Semi-Interpenetrating networks of CBM:** The development of interpenetrating networks of CBM involves creating a 3-D structure where two or more polymer networks whereas the semi-interpenetrating polymer networks are materials in which one polymer network is formed within the pre-existing structure of another polymer networks. These approaches are often used to enhance the material's mechanical strength, stability and different characteristics by tailoring domains of material with an introduction of new material depending upon the application of the material. The researchers from the USA, China and Vietnam investigated the sensitive detection and efficient adsorption of Cu(II) and Cr (VI) using fluorescent carbon dots crosslinked cellulose nanofibril-chitosan interpenetrating hydrogel system in which these findings showed that CNF/CS gel has high adsorption capacities of 148.30 and 294.46 mg/g, respectively, and matched both the pseudo second order and Langmuir

model [83]. The researchers from Thailand worked on the clickable crosslinked interpenetrating network for developing persistently reversible pH/thermo-responsive chitosan/poly(N-isopropylacrylamide) hydrogel [84]. The resulting hydrogel exhibited a consistently reversible pH and thermo-responsiveness, as demonstrated by its ability to retain its appearance and preserve its dimensional stability, including its mechanical strength, even after several cycles of heat and pH treatment [84]. The development of semi-interpenetrating hydrogel comprising of chitosan, acrylic acid and thiourea by our research group using solvothermal synthesis which was further investigated for controlled release of organophosphate pesticide and triazophos in which the hydrogel was developed by optimizing different parameters such as concentrations of acrylic acid, $K_2S_2O_8$ and thiourea and solvent volume [85]. It resulted in a maximum release of 53% after 25 days at pH 6 and the value got lowered under acidic and basic conditions which helped in surface and groundwater contamination [85]. In similar work by our group, the cadmium was removed from an aqueous solution by hydrogel developed from microwave synthesis in which it was investigated in terms of percentage swelling (P_s) under optimal circumstances it had a percentage of grafting (3845%) and swelling (311%) [86]. In addition to that, it showed 98.1 % removal efficiency of Cadmium ions from a 100 mg/L solution and showed a regeneration efficiency up to eight cycles but in the twelfth cycles it showed a decrease of 40% [86]. The development of semi-inter penetrating polymer network with carboxymethyl chitosan in which the effect of carboxymethyl chitosan content on different characteristics such as thermal stability, mechanical, surface wettability and particle size distribution in the dispersion was investigated [87]. It was demonstrated that with the 80% biomass contents of the resultant films and the outstanding storage stability of the composite dispersion because of the growing hard component of the films and the potent hydrogen bonding interaction between polyurethanes and carboxymethyl chitosan, there was a noticeable rise in the crosslinking density and glass transition temperature of the composite films as chitosan content increased [87].

II. SUMMARY

In summary, CBMs are becoming an increasingly prevalent subject in both academia and industry. This chapter primarily discusses the categorization of CBM according to factors like the type of crosslinker, initiator, monomer and physical or chemical modification employed in its synthesis, with emphasis on the various methods employed and the applications of CBM in diverse fields. Furthermore, it provides a summary of the synthesis process for various CBMs, including hydrogels, nanoparticles, sponges, beads and interpenetrating and semi-interpenetrating networks with emphasis on various characterization methods to verify the properties of the synthesized CBM.

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