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Sustainability Spotlight Statement:

Environmental pollution remains a pressing global issue, posing significant risks to ecosystems and human health. Addressing this challenge is crucial for ensuring a sustainable future. Our review, "Modernizing Environmental Cleanup: Harnessing Greener Nanobiopolymers for a Sustainable Tomorrow," explores innovative, eco-friendly nanobiopolymers as advanced solutions for remediation. These materials offer efficient, non-toxic alternatives to conventional methods, significantly reducing environmental impact. By leveraging cutting-edge technology, our work aligns with the United Nations Sustainable Development Goals (SDGs) 6 (Clean Water and Sanitation) and 9 (Industry, Innovation, and Infrastructure), promoting sustainable practices and fostering a healthier planet.

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Greener Nanobiopolymers and Nanoencapsulation: Environmental Implications and Future Prospects

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Abstract:

To minimize the consumption of nonrenewable resources and ensure environmental sustainability, there ought to be greater utilization of abundant and renewable greener nanobiopolymers, particularly those derived from various plants and microbes. This article discusses the various types, origins, and synthesis methods of biopolymers, including those that come from natural resources and microorganisms, with a focus on their properties in nano format; the most common and recently researched nanobiopolymers have been deliberated. In addition, discussion on various synthesis steps and structural characterization of green polymeric materials like cellulose, chitin, and lignin is also incorporated. A comprehensive discussion of greener nanobiopolymers with illustrative examples has been covered for the last five years comprising their diverse types and topologies including the environmental improvements realized via the deployment of nanoencapsulation, especially the appliances of polymer nano encapsulated materials in wastewater and soil treatment. The emphasis on the use of greener nanobiopolymers for sustainable environmental remediation is specifically highlighted for the decontamination of soil, water, and air with the main objective to offer an overview of their adaptability embracing nanotechnology. This effort could stimulate additional research in their deployment in practical environmental appliances.

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Keywords: biopolymers, environment, green, nanoencapsulation, nanotechnology, remediation, sustainability

1. Introduction

Year after year, environmental pollution continues to rise and is now considered one of the most critical issues that society faces, causing irrevocable damage. Despite being a long-standing challenge, environmental pollution has become a significant problem as a result of ongoing urbanization and the incessant development of industry around the globe. The growing human population, vehicles, industrial smoke, and other essential components of modern life have increased our use of natural resources to the fullest, contributing to the degradation of the environment. Hazardous substances, such as toxic heavy metal ions, leftover pharmaceutical compounds or their metabolites, pathogens, various classes of sulfur compounds, or other chemicals dispersed in the air, soil, or water, pose a threat to both human health and the ecological system even at low concentrations. Thus, the search for a sustainable solution to address the degradation of the environment has become increasingly important with continuous search for cost-effectiveness and eco-friendly solutions.[1] However, the challenge of eliminating toxins in an environmentally friendly and cost-effective manner using readily accessible technology remains a challenge.[2][3] Many conventional techniques for environmental clean-up involve the consumption of chemicals and the generation of toxic by-products that are hazardous to the environment.[4][5] Numerous techniques namely adsorption, ion exchange, chemical precipitation, membrane-based filtration, photodegradation, solvent extraction, and reverse osmosis, are available for the treatment of pollutants. Nanotechnology, a powerful emerging technology of the 21st century, can help assist in the sustainable development of solutions for social communities. The unique properties of nanomaterials, such as their surface area, size, and reactivity, have enabled the development of novel, high-tech materials, such as nano sorbents, which are more efficient and faster in accomplishing wastewater remediation than traditional materials. Particularly, due to their new physical and chemical characteristics—which differ significantly from that of bulk phase—and their relatively small size (generally ranging from 1-100 nm in diameter), high surface-to-volume area, catalytic activity (in the form of adsorption), efficient interfacial reactions, and specific functions, nano materials are being developed into newly miniaturized, precise, and highly sensitive nano sensors.[6] Biopolymers are polymers that

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are naturally synthesised by the cells of living organisms and often comprise monomeric units that are covalently bonded to form larger structures. The related polymer nanocomposites exhibit markedly improved properties compared to their individual counterparts.[7][8] In the design of such polymer matrix nanocomposites, a variety of natural or synthetic polymers are employed due to their remarkable chemical structure, low weight, ease of processing, and recyclability; however, they lack mechanical and thermal stability.[9] Polymers could be introduced in nanocomposites as a polymeric species, or as a monomer, which could be polymerized via an in-situ mechanism. In order to improve their properties, large numbers of additives known as "nanofillers" are added to polymeric matrices. Recent developments in the generation of nano biopolymers from living organisms have generated a great deal of interest in several scientific and technical fields.[10]Unlike synthetic polymers, which are made from petroleum, these nano-based materials are renewable and environmentally friendly. Biopolymers, also referred to as organic plastics, are manufactured from renewable biomass namely corn starch, pea starch, and vegetable oil, among others. By placing more emphasis on the utilization of such biopolymers, it is possible to conserve fossil fuels which will in turn reduce CO_2 emissions and thus help support sustainable development. These All aterials are machinable due to their unique nano-dimensional effects such as ultra-high aspect ratio and length-to-diameter ratios. Nano bioremediation offers an excellent alternative for removing pollutants by utilizing nano biopolymeric composites.[11–13]

The present article discusses the application of various bionanopolymeric materials, for the general remediation applicable to water, soil, and air pollutants. Assorted processes for the removal of heavy metals and dyes, and other aspects namely the need for air filter masks, comparison of current air filters and traditional counterparts, and the clogging effect of biopolymers over various other soil treatment methods, are deliberated. All these factors govern the need for specific biopolymers in assorted environmental domains. A quantitative methodology for evaluating the environmental impact of nanobiopolymer isolation technologies is offered via life-cycle assessment encompassing crucial steps namely goal and scope definition, life-cycle inventory modelling, life-cycle impact assessment, and interpretation which are among the first three steps.[14] **Fig. 1** presents the life cycle assessment process for nanobiopolymers.

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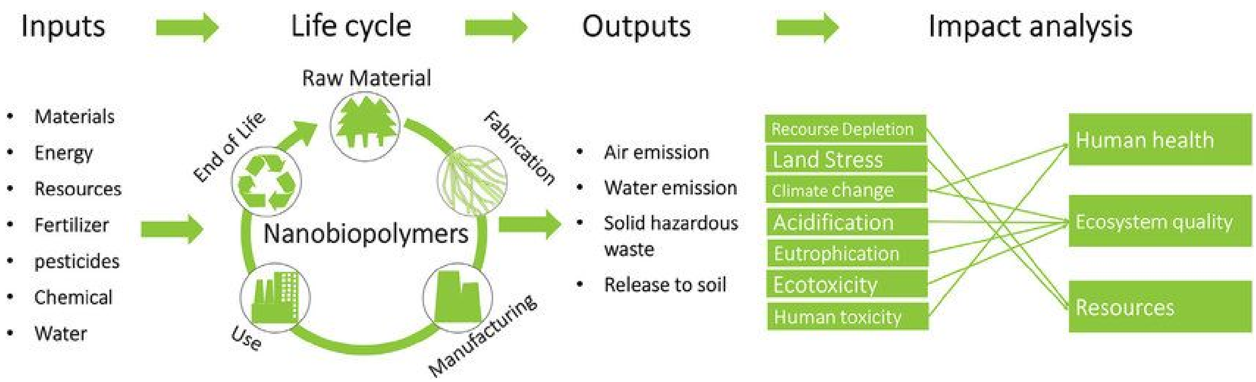

Fig. 1: Life cycle assessment for nanobiopolymers. Copyright (2018) Wiley. Used with permission from (Nanobiopolymers Fabrication and Their Life Cycle Assessments).[14]

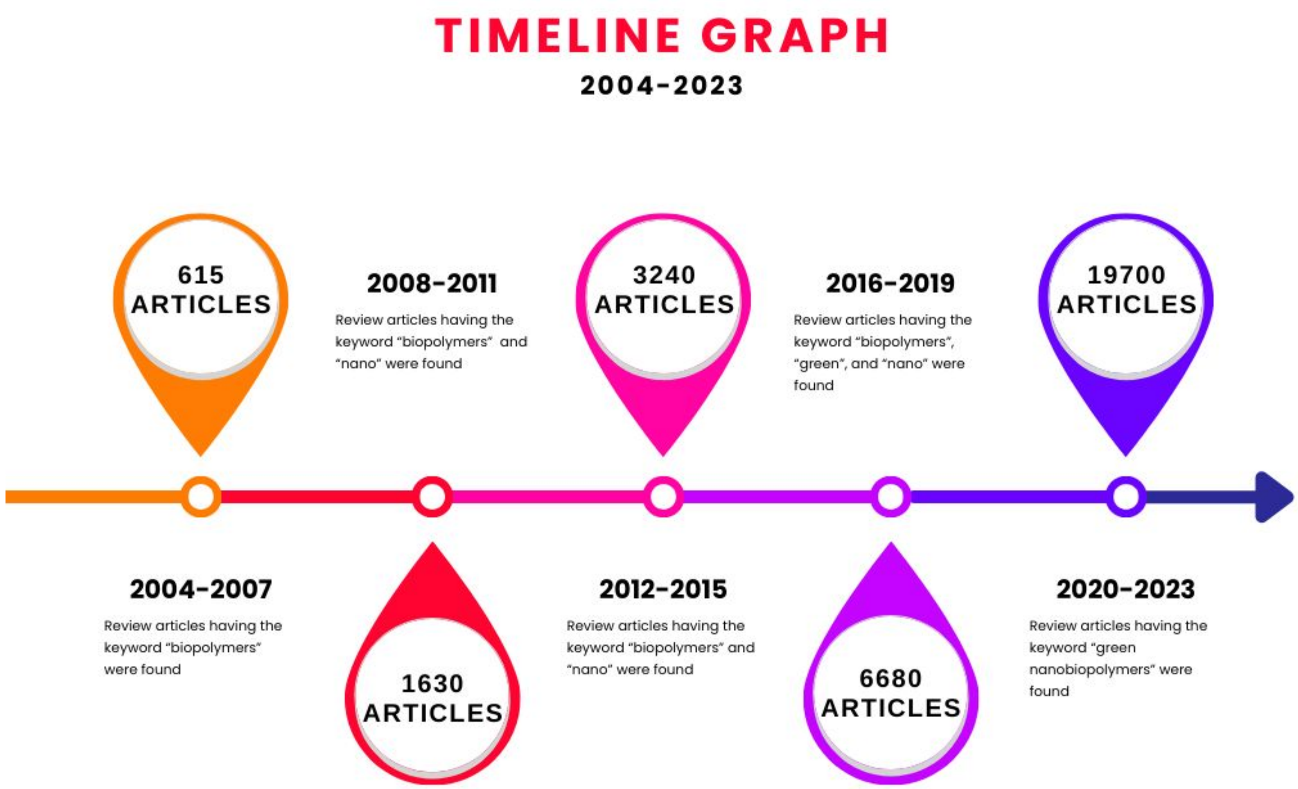

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Fig. 2: Depiction of the number of publications that include the keywords “biopolymers”, “nano”, and “green nanobiopolymers” which were uncovered, from the year 2004-2023, acquired from Google Scholar

Fig. 2 reveals the extent of the growing field of biopolymers, nanobiopolymers, and finally, greener nanobiopolymers, in terms of their publications. The prominent rise in the number of articles every 4 years is an indication of the growing usefulness and popularity of green nanobiopolymers, owing to their various attributes like adaptable design and modification based on the requirements of the current scientific and industrial demands. The biopolymers are ascertained to be biocompatible, biodegradable, and good adsorbents, making them useful in a variety of appliances, including edible films, emulsions, packaging materials, medical implants, and environmental pollution remediation.

2. Biopolymers

The phrase "biopolymer" can be used to refer to the class of polymers that are made up of monomeric units that are covalently bonded to form oligomeric substances and are typically obtained from biological sources, such as plant, animal, or plant-based origins; "bio" means the material is created by living things.[15] Materials originating from plant or animal sources, such as vegetable oil, sugar, fat, resin, protein, amino acids, and others, are examples of biopolymers.

The differentiation of biopolymers from synthetic polymers is through their sophisticated molecular assembly, which takes on a clear-cut, well-defined 3D shape and structure with their functionality in vivo. Renewable biopolymers offer an alternative to polymers derived from fossil fuels, as they are often created from starchy substances, sugar, natural fibers, or other organic, biodegradable elements and are amenable to decomposition upon exposure to microorganisms from compost, soil, or marine environment.[16]

2.1. Types of Biopolymers

Biopolymers can be divided into several subgroups according to different contents, origins, and sizes **(Fig. 3)**. They can be classified on the basis of their origin: i) natural biopolymers, ii) synthetic or man-made biopolymers, and iii) based on repeating units.

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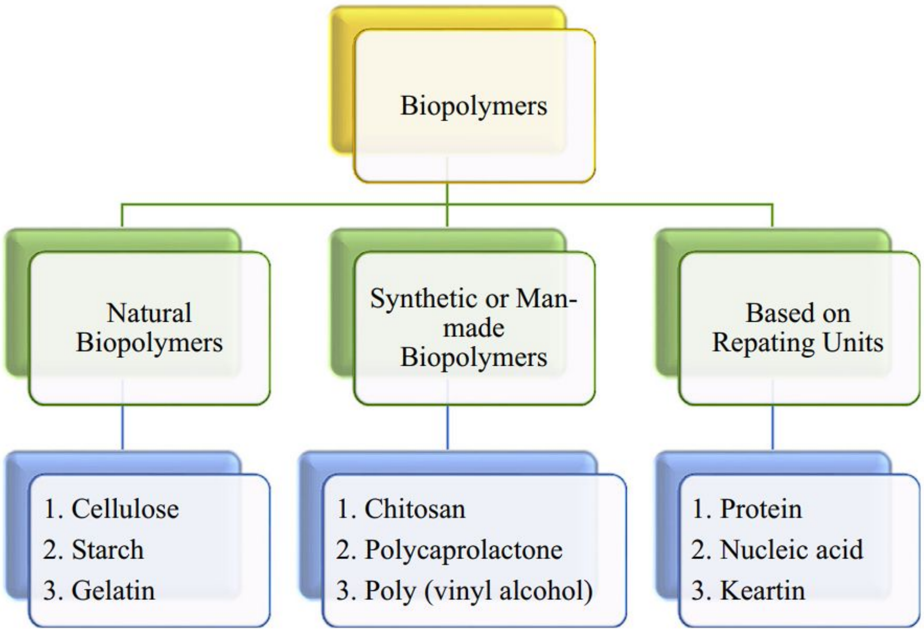

Fig. 3: Different classes of biopolymers.[17] Reproduced from [Biopolymers and their Industrial Applications], with permission from Elsevier)

2.1.1. Natural Biopolymers

Natural biopolymers are polymers found in nature that regulate different aspects of an organism's life cycle. Among many of the favourable qualities are their non-toxicity, biodegradability, and biocompatibility as exemplified by discussion on cellulose, starch, and gelatine.

2.1.1.1. Cellulose

The first thermoplastic polymer identified in plants is cellulose with chemical formula $(C_6H_{10}O_5)_n$, where n is the number of cellulose's repeating units.[18] Cellulose is known by the IUPAC name (6,5)-2-(hydroxymethyl)-6-(3-S-4,5,6-trihydroxy-2-(hydroxymethyl)oxan-3-yl)oxyoxan-3,4,5-triol.[19] It is a polysaccharide with a linear structure made up of 100-1000 (1-4) b-linked glucose units repeating units.[20] The glucose unit with (1-5) OH and CH_2OH groups in the same plane is called D-glucose. Strong intra- and intermolecular hydrogen bonds exist between the oxygen atom and the hydroxyl group of the D-glucose unit. It is crystalline in nature, has a high molecular weight, and varies in Dp ranges between 8000 and 10,000 dpi. It serves as a structural element in plants' main cell walls.

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2.1.1.2. Starch

The starch is the main energy source with 60% to 75% of its weight made up of grain products consumed by humans.[21] Its structure is similar to cellulose's, but its internal bonding is different.[22] It finds use as a thickening agent, adhesive, and moisture retention material in numerous applications.[23] and is a homopolymer of D-glucopyranose units that are connected by α-(1/4) and α-(1/6) glycosidic bonds. A D-glucopyranose molecule is created when the C_1 and C_4 or C_6 carbons of the glucopyranose ring combine.[24] Because of the aldehyde group, starch molecules have one free reducing end. Amylose and amylopectin are the two forms of starch, amylopectin being a larger molecule with a highly branched structure, while amylose is an essential carbohydrate with a linear assembly. Generally speaking, plant cells use a complicated biosynthesis pathway that is regulated by enzymes to produce starch. In green photosynthetic tissues, the chloroplasts are the site of starch biosynthesis.

2.1.1.3. Gelatine

Gelatine is a naturally occurring biopolymer obtained from the meat industry, which is derived from raw collagen. Collagen, hydrolysate, and denatured collagen are other terms for gelatine. It has eighteen different kinds of essential amino acids that are included in a normal diet. It is created through the hydrolysis of raw collagen found in many animals connective tissues, including skin and bones.[24] Based on method and composition, there are two types of gelatine. Raw collagen is hydrolyzed in the presence of acid to produce type-A gelatine 18% of it being nitrogen. Alkaline hydrolysis of collagen, which has 18% nitrogen atoms without the amide group (-CONH-), produces type-B gelatine. At both high and low temperatures, it is a temperature-sensitive biopolymer; at elevated temperatures, it melts and forms into a coil and shapes as a coil-to-helix at lower temperatures. Because of the reactive groups (like -CONH-, -SH-, and -COOH-), it can be altered in the form of nanocomposites. It can form hydrogels, which are used in biomedical applications, and has a special crosslinked attribute. Gelatine is used to speed up the healing process following sports injuries and also for enhancing the quality of hair.

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2.1.2. Synthetic or Man-Made Biopolymers

Synthetic nanobiopolymers are polymers that have been modified from natural nano polymers or chemically synthesised from artificial monomers such that they can degrade naturally without generating hazardous residues in the living and natural surroundings.[25] Synthetic nanobiopolymers have garnered a lot of interest in recent years due to their unique advantages over natural nanopolymers in terms of stability and flexibility for a wide range of applications.

2.1.2.1. Chitosan

The largest structural polysaccharide based on nitrogen, chitosan is composed of repeating modified glucose subunits and is found in acetylated form as chitin among fish, insects, and many other vertebrates. Chitin's organisation resembles that of cellulose because monomer units have hydroxyl and amine substituents wherein a methyl amide group takes the place of the hydroxyl group.[26] Living things and vertebrates may readily digest it because it is created by organisms.[27] The fibrous chitin can be broken down into smaller constitutional glucose units by symbiotic bacteria and protozoa.

2.1.2.2. Polycaprolactone

Polycaprolactone (PCL) with (1,7)-polyoxepan-2-oneass the IUPAC name, is a biopolymer of synthetic polyester and is created by polymerising caprolactone through ring opening in the presence of a catalyst, like stannous octate. and finds utility in biological contexts.[28] In order to reduce cost, boost biodegradability, and enhance impact strength, it is also added to starch. Some of the special qualities of PCL, include its high toughness, biocompatibility, and cost-effectiveness. Compared to other biopolymers, PCL degrades considerably more slowly[29] and its special characteristic makes it useful for drug delivery applications. Because of its hydrophobic nature, it has strong chemical resistance towards biological fluids. It combines seamlessly with other man-made polymers. In view of the easy cleavage of it ester bond, PCL readily breaks down and is often deployed as a biomaterial in tissue-engineering applications.

2.1.2.3. Polyvinyl Alcohol

Polyvinyl alcohol (PVA) is a thermoplastic biopolymer that is produced through the hydrolysis of its precursor, polyvinyl acetate and can be degraded by biological microbes being very soluble in water. [30] PVA is employed in the production of numerous polymer end products, including food packaging, liquors, and surgical threads. It is an extremely flexible, ductile, and robust polymer. The physical and chemical characteristics of PVA are based on grade, molecular weight, and the

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percentage of degree of hydrolysis. Its gas barrier qualities, flexibility, and tensile strength are all outstanding attributes.[31] This biopolymer is highly prevalent and has the ability to form chemical bonds with many surfaces, including water. PVA is a biodegradable and nontoxic polymer and is often used in food packaging and in the biomedical fields as wound dressing, medication delivery, cardiac surgery, and contact lenses.

2.1.3. Polymers Based on Other Repeating Units

2.1.3.1. Protein

Proteins are necessary building blocks for human daily existence[32] and comprise fundamental components that make up bodily tissues. Peptide bonds allow the individual amino acids that make up proteins to be conjugated and are created via the combination of amino and carboxylic groups. [33]A polypeptide bond holds the lengthy protein macromolecular chain together as proteins are essential for numerous biological functions including as catalysts for the movement or storing of other molecules (oxygen). They also give the immune system mechanical support, keratin being the primary example of a protein.

2.1.3.2. Keratin

A protein polymer called keratin that is found in horns, claws, and hooves and is a combination of floating proteins, enzymes, and many keratinized filaments.[34] It is described as a specific filament-floating protein with superior physiochemical characteristics. often derived from cells and tissues. Keratins are generally divided into two categories:

i. Primary keratin: This keratin, which includes K8/K18, is generated from both stratified and epithelial cells.

ii. Secondary keratin: Other byproducts are used to make these epithelial cells; K_7 and K_{19} being the examples.[35]

Keratins are found in fibre connections, cellular binding, and are frequently used in biological applications like cell adhesion. In the cosmetics industry, they are utilized as skin care ingredients, fertilisers, and sites for cellular attachment.

2.1.3.3. Nucleic Acids

RNA is the earliest known biomolecule which stores and transfer the information contained in cells. All portions of polymeric chains, including genes, require DNA to store genetic information[36] where every nucleic acid component is essential for transmitting the genetic

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information. Nucleotides are tiny monomeric components that make up this polymer.[37] Three components make up each nucleotide monomer: a phosphate group, a nitroglycogenous base, and two types of pentasugars namely ribose and deoxyribose sugar that are present in the natural world.

2.2. Sources and Synthesis of Biopolymers

As mentioned earlier, bio-based polymers are substances that are composed of replenishable resources as exemplified by agricultural products like corn, potatoes, and other plants rich in carbohydrates. Due to significant technical breakthroughs, the emphasis is now placed on resources other than those derived from food. [38] Polymeric biopolymers are also created synthetically with a variety of appliances through novel developments via plant engineering. [39]

These polymers are produced in bulk and then moulded for specific end uses. In addition, a variety of biopolymers, such as polyesters, polyamides, and polysaccharides, which are used to create everything from plastics to viscous solutions, depend on microbes for their production. Their physical characteristics rely on the molecular weight and contents of the polymer.

2.2.1. Biopolymers derived from Natural Plant Resources: Polysaccharides

Polysaccharides are composed of complex carbohydrates that are widely present in nature or the environment and serve as structural components in both, plants as well as animals. The three most common biopolymers derived from natural plant resources are starch, chitosan, and cellulose. Starch is a large polysaccharide and is the most prevalent and dominant polysaccharide in nature. Natural starch is frequently found as a granular substance that can be processed using customary methods for making plastics or used as a filler for polymers including as a drug delivery agent in tissue engineering applications, microcellular foams, and the food industry. Its main drawback is its hydrophilic nature, which limits its application in environments with high moisture content. Starch can be coupled with biodegradable polymers like polyvinyl alcohol (PVA), polycaprolactone (PCL), chitosan, and others to generate fully biodegradable materials. Due to its biocompatibility, biodegradability, low toxicity, wide availability, and affordability, chitosan, the most exceptional biopolymer is generated by deacetylation of naturally abundant, chitin, and is often deployed in drug delivery systems. Because of its reactive amino and hydroxyl functional

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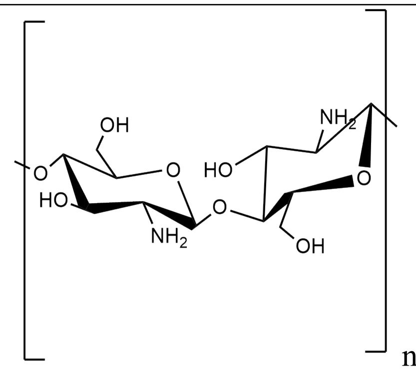
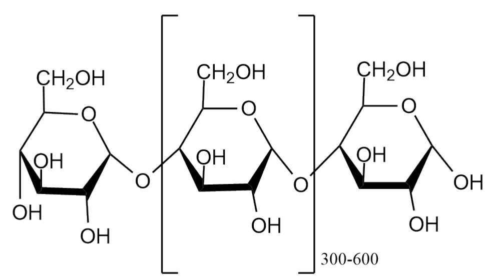
groups, chitosan can be combined with other polymers to enhance their functional characteristics through inter- or intramolecular crosslinking in the polymer matrix.[40,41]

Cellulose, a vital biopolymer that is abundantly present in our environment in plant cell walls, is another important candidate. High sorption capacity, biocompatibility, biodegradability, relative thermostability, mechanical toughness, and adjustable visual appearance are only a few of its fascinating properties. Not surprisingly, numerous industries utilize cellulose in various ways as exemplified by the formation of bio-composites. Some leading examples of polysaccharides are presented in **Table 1**.

Table 1: Prominent examples of Polysaccharides.

Name	Chemical formula	Structure
Chitosan	$C_{56}H_{103}N_9O_{39}$	
Starch	$(C_6H_{10}O_5)$□	

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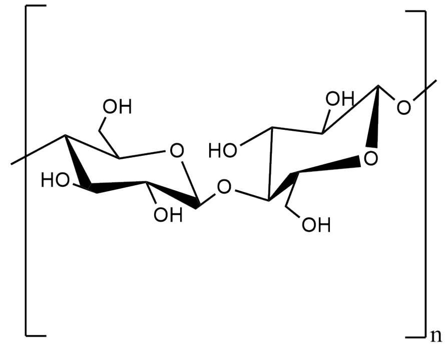
Cellulose	$(C_6H_{12}O_5)_n$	

2.2.2. Biopolymers derived from Natural Animal Resources: Proteins

For a variety of hierarchically complex biological material scales, proteins are crucial building blocks which are essentially polypeptide-based polymers created by condensation polymerization of amino acids; keratin, collagen, casein, and fibroin are significant animal proteins. Collagen is a protein that is abundantly found in the extracellular matrix of vertebrate animals and is employed widely in the food and pharmaceutical sectors. Collagen fibrils offer the main mechanical support and structural organization of connective tissues and they find predominant applications in areas like wound healing, cosmetics, along tissue engineering.[42]

The main challenge and opportunities in biopolymer research and developmental endeavors is to find acceptable modification pathways to improve the properties of natural polymers as exemplified by the production of natural polymers based on proteins or wheat gluten.[43,44] Due to its excellent thermoplastic qualities, superior processability, and amazing biodegradability, wheat gluten, a by-product of the starch industry with high protein content, could be regarded as an ideal candidate for many applications. Some leading examples of animal proteins are listed in Table 2.

Table 2: Examples of Animal Proteins.

Name	**Chemical Formula**	**Structure**

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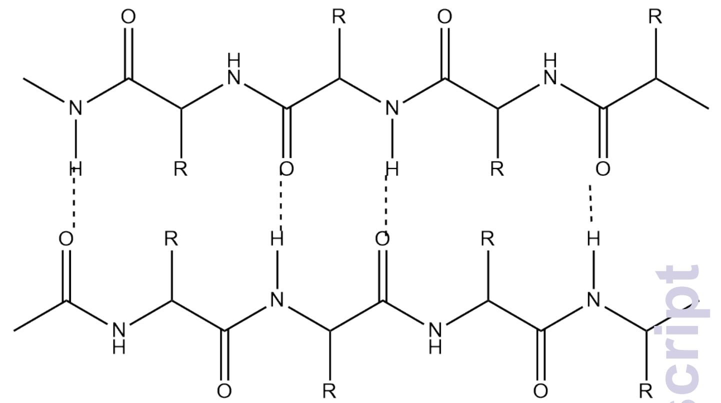
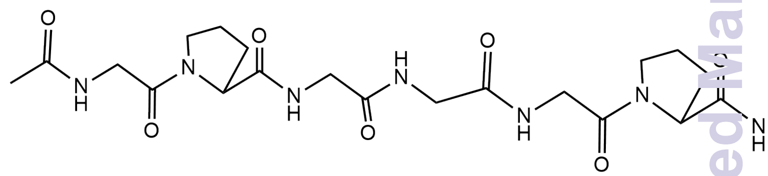
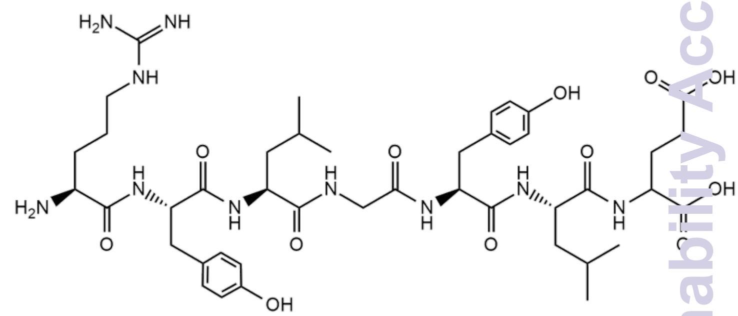
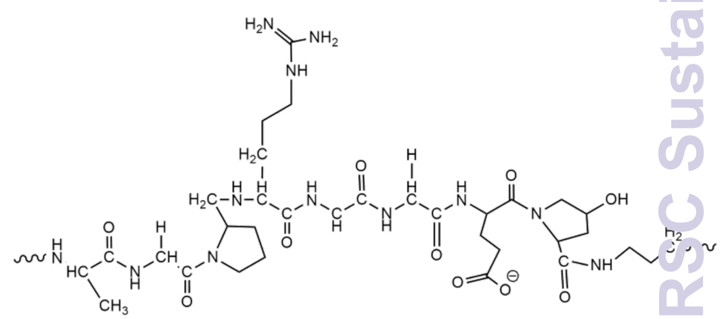
Keratin	(Gly-X–Y) $_n$	
Collagen	$C_4H_6N_2O_3R_2$	
Casein	$C_{81}H_{125}N_{22}O_{39}P$	
Gelatin	$C_6H_{12}O_6$	

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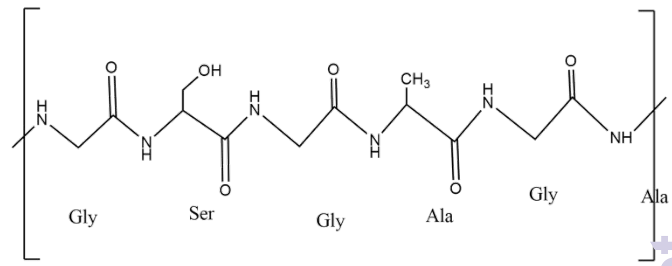
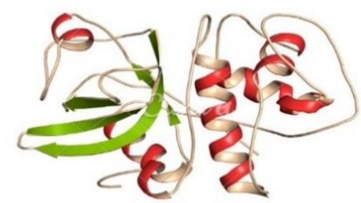
Fibroin	**(**Gly - Ser -Gly- Ala -Gly-Ala**)$_n$**	
Whey protein	The proteins consist of α-lactalbumin, β-lactoglobulin, serum albumin and immunoglobulins	

2.2.3. Biopolymers Obtained from Microorganisms: Polyesters

Microorganisms produce a wide variety of biopolymers, such as polysaccharides, polyesters, and polyamides, which vary from viscous solutions to plastics with their physical properties being defined by their molecular weight and composition. The genetically modified bacteria are especially suitable for high-value medical applications like drug delivery and tissue engineering which is facilitated by the alteration of various biopolymers produced with the assistance of micro-organisms.[45]

Microorganisms require a certain set of nutrients and a controlled environment to produce biopolymers which can be accomplished chemically via the polymerization of monomers; they can be created often through fermentation as well. A higher proportion of biopolymers of bacterial origin are biocompatible and have no harmful effects on biological systems as they are synthesized either as a part of their defense mechanism or for storage purposes.[46,47]

Algae are among the microorganisms that offer suitable feedstock for manufacturing plastic in view of their high productivity and adaptability to varied environmental conditions. It is now possible to employ algae to consume carbon and lessen the impact of greenhouse gas emissions

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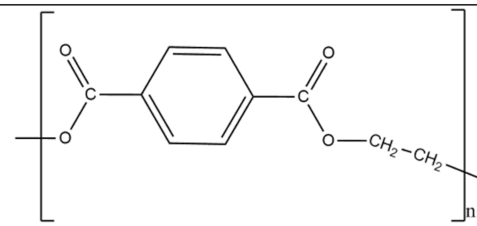
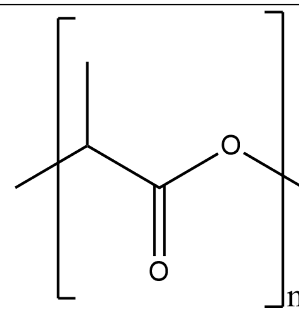
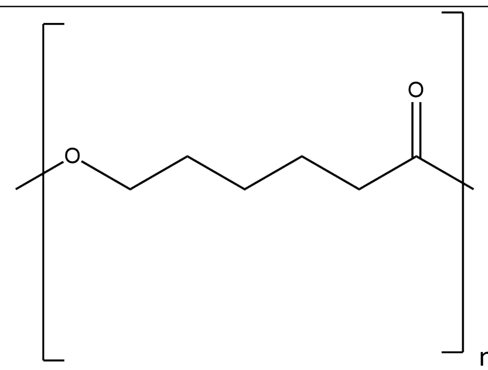
from manufacturing facilities and power plants. In the era of bioplastics, algae-based plastics have become more popular relative to conventional techniques that employ corn and potatoes as plastic feedstocks. The leading examples of polyesters are presented in **Table 3**.

Table 3: Some examples of Polyesters.

Name	Chemical Formula	Structure
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	
Polylactic Acid (PLA)	$(C_3H_4O_2)_n$	
Poly(e-Caprolactone) (PCL)	$(C_6H_{10}O_2)_n$	

2.3. Biopolymers-Advantages and challenges

The most intriguing features of biodegradable polymers are their ability to survive a variety of environmental conditions and their disposability in the presence of bioactive molecules. Due to their expanding appliances in environmental safety, packaging, biomedical implementation, and agricultural usage, biodegradable polymers play an extraordinary role. In view of its readily

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hydrolyzable ester linkages along with economical manufacture, poly (lactic acid) (PLA) is one of the most readily available and widely deployed polyesters. According to Rasal et al.'s [48] research, the manufacture of PLA uses 25–55 percent less energy as compared to that of polymers derived from petroleum, albeit this figure may increase in the near future. Consequently, there is now more interest in producing lactic acid through fermentation using renewable resources rather than petrochemicals as the biotechnological pathway offers many advantages over chemical synthesis. Given that they are disposable and produced using sustainable resources, biodegradable polyesters can be considered as a potential material to help with the problem associated with the disposal of solid waste. These polyesters' low immunogenicity and biological origin make them ideally suitable for usage in food packaging as well as other consumer goods.[49]

Despite the fact that biodegradable polymers have numerous uses, some of their properties, such as brittleness, low heat deflection temperature, low melt viscosity, poor thermal as well as mechanical resistance, and slow degradation rate, limit their deployment in industrial settings. The aforementioned drawbacks can be resolved, however, by improving the material's thermomechanical characteristics through various means such as copolymerization, mixing, and the use of fillers. Another notable downside of biodegradable polymers is the cost-effective manufacturing and recovery of biopolymers through the fermentation process as it is limited by the cell's ability to utilize inexpensive carbon sources, especially agricultural waste products. Since microorganisms grow slowly in agricultural waste or on inexpensive mediums, fewer polymer-plastic technologies and materials are created, which boosts the cost of downstream processing. It is crucial to isolate and screen potent and efficient microorganisms (especially fungal and bacterial strains) from the natural environment to employ relatively inexpensive feed stock. In order to reduce production costs and achieve the best productivity under optimum conditions, research has now focused on culture strategies to expand growth media using affordable carbon substrates.[50]

3. Greener nano biopolymers

Organic compounds made from naturally replenishable resources include nano forms of biopolymers as well. They are widely distributed in nature as well and they arise via biological monomer chain reactions. Because of ease of production and economical, they are employed in ecologically sensitive applications. In natural systems, polysaccharides often comprise the most prevalent biopolymers and they are made up of sugar monomers which are further connected by

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glycosidic linkages. They perform a variety of crucial tasks in living things, encompassing supporting the structure, providing energy, as well as facilitating the transition of certain cells; cellulose, starch, chitin, and silk are nano-biopolymers that can be produced via metabolism.

3.1. Types and structural properties of greener nano biopolymers

3.1.1. Nanocellulose

Cellulose, the most prevalent polymer on earth, is made by plants, microorganisms, and cell-free systems, and chemically, it consists of repeating β-D-glucose monomers held together by β-(1,4)-glycosidic bonds. Natural cellulose usually has a fibrous form with interspersed crystalline and amorphous parts. Nanocellulose, also known as cellulose nanocrystals (CNC), cellulose nano whiskers (CNW), and cellulose nanofibers (CNF), is produced by fiber separation and occurs in a variety of morphologies. Microbial cellulose, also known as bacterial nanocellulose (BNC) and acellular cellulose, is the cleanest type of cellulose available compared to plant cellulose, which contains lignin and hemicellulose as additional components.[51],[52] Nanocellulose possess characteristic structural, physicochemical, mechanical, and biological features such as a three-dimensional reticular network fibre structure, hydrophilicity, biodegradability, good mechanical strength, biocompatibility, high crystallinity, light transmission, high specific surface area, multi-functionality, and its ability to be molded into complex three-dimensional shapes.[53] Nanocellulose is a sustainable material that can be produced using cell-free systems, various microbial strains, and the degradation of plant and animal cellulose. Nanocellulose is widely deployed in a variety of fields as a tuneable material, both on its own and in composite form with other materials; usage includes tissue engineering, wound dressing, textiles and clothing, cosmetics, bioprinting, regenerative medicine, energy, optoelectronics, environmental remediation, among others.[54],[55]

The structural qualities of nanocellulose are better than those of microcrystalline cellulose (MCC), in terms of high mechanical strength and its ability for easy surface-modification using a variety of techniques. This is in view of a higher concentration of hydroxyl (OH) groups, rendering it more hydrophilic and amenable to various chemical and physical modifications. Nanocellulose has thus garnered a lot of attention as the ideal nanostructure for creating novel, high-value nanomaterials due to its excellent biocompatibility, high mechanical strength, renewability, and low cost.

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3.1.2. Nanochitin

Like cellulose, chitin is a natural polymer that occurs abundantly in nature. Many terrestrial arthropod creatures, including insects and spiders, have exoskeletons made of a polysaccharide called chitin, which is fuelled by the shells of crabs and shrimp that are consumed as seafood. The chitin molecule ($C_8H_{13}O_5N$) is a long-chain polymer of *N*-acetylglucosamine, a glucose derivative, and has a long-chain structure generated by the repetition of two *N*-acetylglucosamine units joined by β-1,4 bonds.[56] Like cellulose, chitin's structure is made up of nanofibers. The most prevalent types of these protein-embedded nanofibers, which range in size from 2 to 5 nm in diameter and 300 nm in length, are α-chitin and β-chitin.[57] Chitin's application is constrained since it is a hydrophobic substance and is insoluble in most organic solvents. Chitin's deacetylated derivative, chitosan, currently satisfies some of the essential requirements namely dissolution in mildly acidic liquids such as acetic acid. Chitin and chitosan are often utilized in a variety of goods, including natural packaging materials, cosmetics, and food preservatives. Chitosan is a wonderful option for usage in biomedical sectors and has broader applications due to its lower degree of acetylation. There are other nanocomposite materials that can be combined with chitosan and chitin namely strengthening of chitosan with chitin whiskers. This material has better water absorption resistance and tensile strength as a result of the combination of their distinct characteristics. Chitosan may be incorporated into various systems and mixed with other natural polymers.[58]

In terms of structure, nano chitin is an assembly of highly oriented nanocrystals of semicrystalline chitin packed into highly oriented microfibrils or fibril bundles that are held together by Van der Waals forces and hydrogen bonds (H-bonding). Nano meter lateral dimension, tailorable crystallinity, fibrillar or rod-like structure, and other characteristics of nano chitin contribute to its appealing qualities. In the exoskeleton of arthropods, nano chitin is chemically contained by a sheath of proteins and formed into elongated fibrils that are encased in a mineral-protein matrix. Therefore, removing minerals and proteins is an essential process that must be completed before isolating nanochitin, and unlike natural nano polysaccharides, this nitrogen-bearing biopolymer is an essential component of life.[59]

3.1.3. Nanostarch

A well-known carbohydrate, starch bears resemblance to cellulose as well as chitin. D-glucose units comprise the two macromolecules amylose and amylopectin that makeup starch. One of the

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substantial naturally occurring polymers on earth, amylose is a chain with few branches that has an average mass of 370,350 Da.[60] Whereas, amylopectin forms a branch at every 22–77 units of glucose and possesses (1-4) linkage.[61] The biological and physical characteristics of starch are based on its crystal structure which is controlled by branches. Besides this, starch may also accommodate phosphate and lipids, which further depends on the botanical source from which it is derived, and these components might alter the starch's properties through the Maillard process.[62] Starch nanoparticles at the nanoscale have diameters ranging from 50 and 200 nm across. The potential to inexpensively generate starch nanoparticles is closely correlated with the availability of starch in nature. Additionally, due to its biocompatibility as well as its ability to degrade without producing harmful or toxic waste, starch at the nanoscale has a large surface area and thus offers a wide range of applications. However, it is susceptible to a wide range of chemical processes because of the abundance of hydroxyl groups on its surface, [63] a property that enables the utilization of starch nanoparticles in various composites. Starch nanocrystals have become a prominent research topic in recent years because of their intelligibility in degradation as well as their competence for regeneration.[64]

3.1.4. Nanosilk

The natural glycoprotein polymer known as silk fibroin (SF) encompasses an H-chain as well as an L-chain and originates from spiders and silkworms. The morphologies of SF, like films, scaffolds, hydrogels, microspheres, as well as nanofibers, can be very diverse. Due to its excellent biocompatibility, lack of toxicity, ease of degradation, as well as anti-inflammatory properties, this protein-based nanomaterial is particularly well suited for use in biomedical research.[65] Additionally, SF has the ability to inhibit the growth of bacteria and reduce metal ions in aqueous solutions. The scope of the material investigation is restricted because pure silk fibroins have the drawback of completely and quickly mixing in water, but this problem can be resolved by mixing nano-silk with other materials. For the usage of SF, sericin which is a glue-like protein found in silk fibroin, has been implicated in allergic reactions to silk, hence its removal is considered crucial[66] which is later refuted as sericin protein has been shown to be a biocompatible substance;[67] the allergic reaction is ascribed to the mixture of sericin and fibroin. Degumming is a thermochemical procedure that moves apart the proteins fibroin as well as sericin from one another. High glycine content with strong binding in silk nanofibroins results in highly stable-sheet nanocrystals[68] characterized by hydrogen bonds as the main molecular interactions in these

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crystalline layers. Despite their reputation as weak bonds, hydrogen bonds impart silk its stiffness as well as tensile strength. Amazing benefits like self-assembly, as well as self-healing, are offered by weak hydrogen bonding in silk nanofibroins.

3.2. The versatility of greener nanocomposites

Greener nanocomposites are polymers that are basically combined with environment-friendly nanofillers, such as cellulose, starch, chitin, clay, or metal oxides.[69] They differ from traditional nanocomposites in various manners, including price, weight, strength, biocompatibility, and environmental friendliness. They have been deployed in several energy devices such as solar cells, batteries, light-emitting diodes, etc. Energy storage, particularly in capacitors, is one of the principal uses for greener nanocomposites.[70]

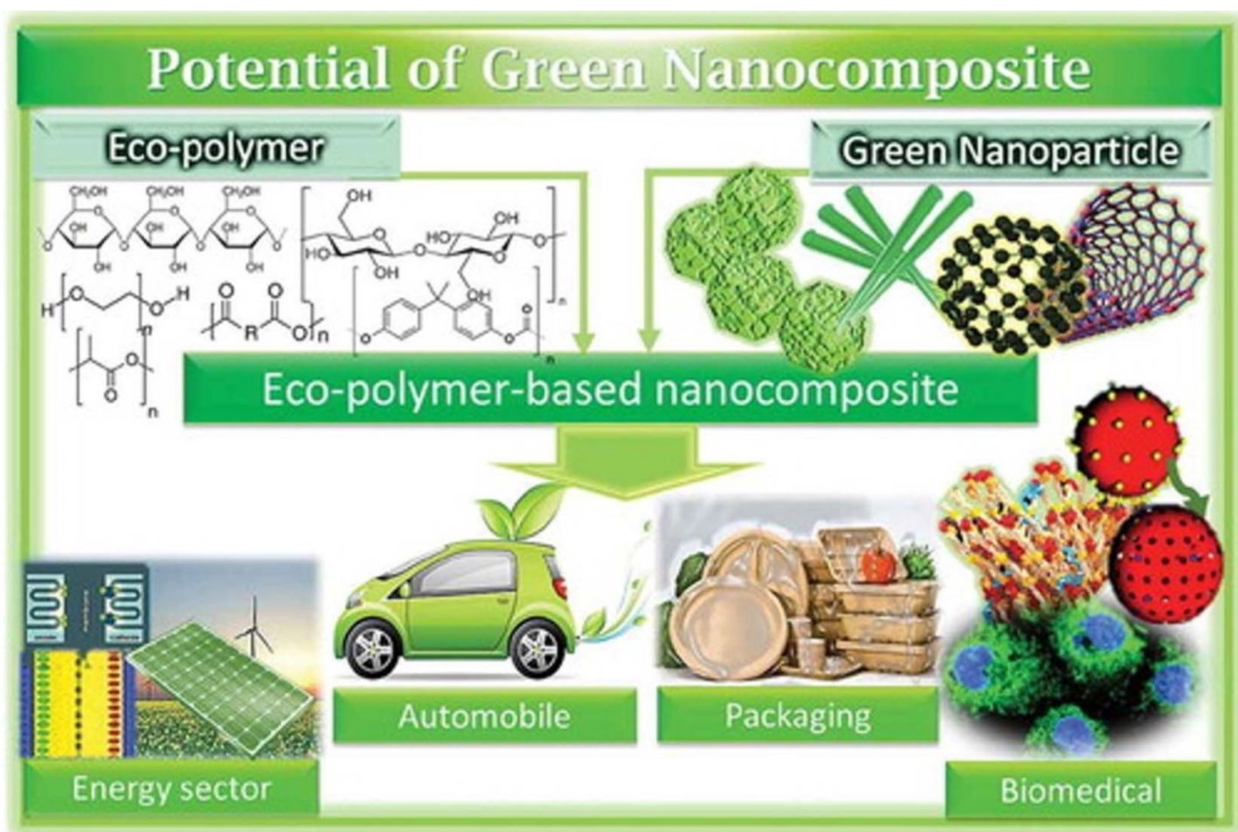

Fig. 4: Applications of polymer-based nanocomposites [11] Reprinted with permission from RSC Advances (2023)

Biopolymer nanocomposites have been a cutting-edge research area in nanotechnology with several fields being the beneficiary over the past ten years. In this context, challenges include (i)

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achieving a resemblance between polymer grids and nano fortifications, (ii) effective detachment pathways for dividing sustainable assets from nano-fortifications, and (iii) appropriate analysis.[71] Cost and energy usage are also significant factors in the commercialization of such products comprising bio-nanocomposites. It is important to note that the most frequently employed method for modifying the properties of biopolymers is the addition of nano-support to the polymer network **(Fig. 4)** although this strategy still needs improvement.[72]

Chitin appears in high proportion as its fibres are employed to make fillers for polycaprolactone (PCL)-based nanocomposites realized via the use of a variety of manufacturing techniques, such as hot pressing and freeze-drying; Ideal stiffness can be achieved with a 2.96 weight % of chitin. [56] Further investigations with FTIR spectroscopy and X-beam demonstrated the presence of chitin in the PVA grid, which was followed by the confirmation of chitin hairs in the conventional flexible lattice. Numerous elements, including elasticity, weight reduction, and diffusion coefficient, further attested to their existence.[73]

Several entities like starch's morphological properties and nanocrystals have been created for conventional elastic combinations. The rates of oxygen and water emission penetrability are also being studied though their effects have been marginal. Starch nanocrystals have expanded water-retaining properties and decreased the cost.[74] Several studies have been published pertaining to polylactic acid (PLA) nanocomposites. The controllable and flexible strength in the KENAF fibrous content was observed to have increased by 50% when the KENAF fiber-based PLA composite in a study wherein the effect of fibre content on the characteristics of PLA was investigated.[75] It has been predicted that the mechanical characteristics of PLA composites will be affected by the KENAF fibre content. Accordingly, the mechanical properties of the PLA network and 30% KENAF fibre-soluble composite were changed. At a 25-weight percent improvement, the polylactic acid (PLA) lattice showed improved mechanical characteristics.

The mechanical properties of a 25-weight % steam-exploded bamboo (SEB) strand infusion from PLA composites were dominant; SEB /PLA strands were twice as strong and solid as PLA strands.[76]

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4. Nanoencapsulation

In recent years, there has been a great deal of interest in the deployment of micro- and nano-sized encapsulation methods which entail encapsulating the desired active material within a carrier matrix or semi-porous membrane. This allows for the transfer of the material between the matrix and a reaction medium, thus enabling the generation of particles with a regulated or trigger-release mechanism; generally, pH, temperature-, and pressure-sensitive agents are employed to control the release of the core material from the encapsulated particles.[77] Various applications, ranging from water treatment and energy storage to agricultural practices, have been using encapsulated materials, particularly in the micro- and nano-size range; improved stability and reusable adsorbents for the removal of pollutants have been observed in water treatment. Subsequently, the applications for encapsulated materials have been extended in various energy storage systems, including phase change materials (PCMs). In the agricultural sector, encapsulated particulates enable the controlled and prolonged delivery of agricultural chemicals at the intended site, as well as the protection of core materials from adverse environmental conditions.[78]

Composite particles are created through encapsulation techniques and typically comprise a core material that has been covered in a valuable secondary material. Depending on the characteristics of the coating, encapsulation may offer properties such as core material discharge in a controlled manner, protection from nonspecific interactions amongst chemicals, convenience of handling and transportation, and ease of separation from matrix to composite particle.

4..1. Components of encapsulation

Typically, encapsulated particles consist of two parts: an inactive polymeric material (shell) and a core active component material that can be in different physical states. The coating material should be compatible with the core material and is often an inert polymer that can be applied to the core material in a desired thickness.[79] Natural, synthetic, and sensitive polymers, created with biological moieties to change their chemical and physical characteristics responsive to internal and external factors, such as pH and temperature, are examples of common coating polymers.[80]

Encapsulated particles can be divided into two main categories based on the core material's dispersion, vesicular and matrix. **(Fig. 5)**.

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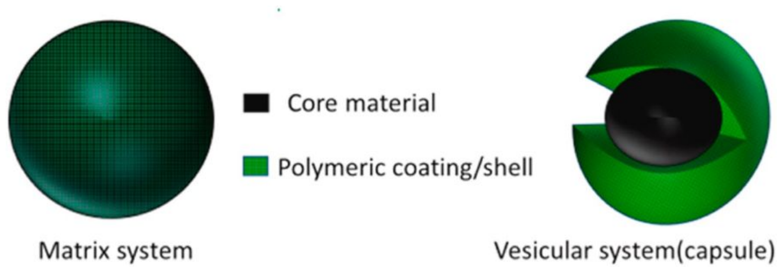

Fig. 5: Visual representation of encapsulation components.[77]

Matrix systems are characterized by the physical and uniform dispersion of the active component, or core. Vesicular systems, on the other hand, are portrayed by the encapsulation of the core within a cavity surrounded by a polymer membrane, also referred to as capsules. Both the terms “matrix” and “vesicular” can be denoted differently, depending on the composition, shape, coating material, and techniques of fabrication **(Fig. 6)**.

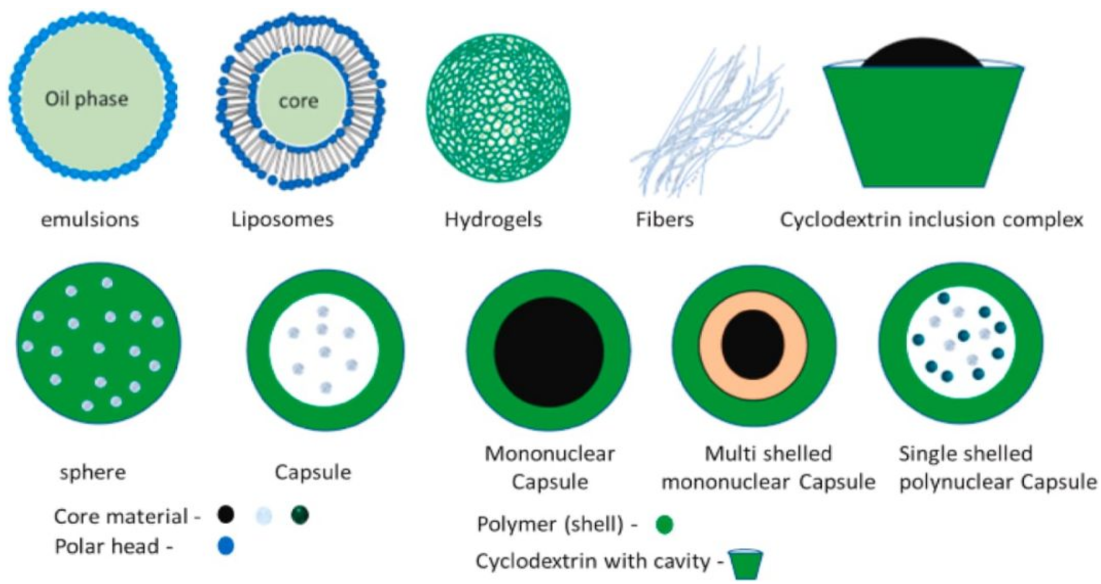

Fig. 6: Visual representation of encapsulated particle types.[77] Reprinted with permission from Elsevier (2023)

4.2. Environmental applications of polymer nano-encapsulated materials

Lately, there has been an increasing interest in the usage of micro- and nano-materials for encapsulation in various environmental contexts, particularly in the areas of water treatment, agriculture, and energy. The use of encapsulation techniques has the potential to significantly

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enhance a number of processes and features in environmental applications, such as the removal of various pollutants like dyes and heavy metals from contaminated water; renewable energy, agricultural processes, and soil treatment for sustained release of herbicide, changes in release property and the soil sorption are some of the additional application avenues.

4.2.1. Wastewater treatment

Encapsulated particles comprise an emerging field of study in wastewater treatment systems.[81] These nanocomposites and materials enable the adsorption and decomposition of various pollutants in wastewater, thus contributing to the sustainability of water use.[82] For example, matrix-based hydrogels, nano-encapsulated membranes, and membranes encapsulated by metals have been deployed in the estimation of pharmaceuticals and heavy metals in wastewater through surface-enhanced Raman Spectroscopy.[83] Recycling of encapsulated materials is an additional benefit of their use in wastewater treatment. For example, alginate-based magnetic beads containing Cyanex 272® have been demonstrated to remove Co^{2+} ions from aqueous solutions with successive 3 times reusability of the adsorbent without altering its initial properties.[84] Additionally, a study demonstrated 67% Sr^{2+} removal from seawater samples.[85] In industrial and textile wastewater treatment, encapsulated bio adsorbents, microorganisms encapsulated in polymeric matrices, have also been used to enhance their performance.[86]

4.2.2. Utilization in soil treatment and agriculture

Encapsulation is a promising technology for agricultural and applications in soil treatment as this sustainable application may include the protection and growth of plants via the encapsulation of bio-active molecules, agrochemicals, and fertilizers, with the aim of delivering them to the intended sites.[87] Additionally, encapsulated polymers, such as absorbent hydrogels and gels, are employed in a variety of forestry, agricultural, industrial, and horticultural applications, as well as in drought management and water conservation.[88] These hydrogels offer a range of benefits, including improved soil quality, water conservation, improved soil fertilization activity, reduced runoff, and enhanced activity of soil microbes. Insect detection and disease detection in plants can also be achieved through the encapsulated nano sensor.[89] Encapsulation also offers eco-friendliness, sustainability, and the controlled release of fertilizer, plant nutrients, and herbicide

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applications.[90] The catalytic and photocatalyst properties of encapsulated materials are commonly deployed for the adsorption and degradative adsorption of pesticides.

5. Environmental Remediation using greener nano biopolymers

Greener nano forms of biopolymers are considered environmentally beneficial because of their biodegradability attributes and they being part of renewable feed stocks.[91] The frequently deployed nanoparticles for environmental remediation comprise single enzyme nanoparticles (SENs), metallic oxides, and zero-valent metals.[92] The abiding interest in metallic nanoparticles (NPs) of iron groups, for example, Co, Cu, Fe, and Ni is due to their magnetic and chemical catalytic properties and hence, these class of NPs and their composites with carbon, silica, polymer and noble metals have found significant applications in environmental remediation endeavors.[93] Also, various other polymeric substances, such as resin, cellulose, chitosan, alginate, carboxymethyl cellulose, etc. are combined with nano biopolymers to enhance their mechanical and thermal properties; nano biopolymers have been deployed for decontamination of water, soil, and air.[94] This usage basically comprises two exclusive environmental domains namely remediation and monitoring.

Eliminating environmental pollutants with nanotechnology: Eliminating pollution has been the biggest environmental challenge[95]as the pollutants in air, water, and soil have detrimental short- and long-term effects. It is imperative to get rid of pollution at the sources of contamination. Nanotechnology has been explored to treat industrial and urban effluents to prevent water pollution, reduce soil pollutants, and decrease many air pollutants in towns and factories to a manageable level.[96]

Nanotechnology-based environmental pollution monitoring: This is conceivable because nanoparticles have fascinating chemical and physical features such as enormous surface area, composition, electrical properties, magnetic properties, mechanical capabilities, and optical qualities. Nano sensors detect contaminants by detecting pollutants' surface markers or by boosting the analytical signal.[97] In comparison to conventional procedures, these unique characteristics of nano sensors are reliable for the sensitive detection of extremely low quantities of contaminants. [98]Scientists have expressed a curiosity in developing nanomaterials-based biosensors for

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detecting environmental pollutants such as heavy metals, pesticides, and bacterial infections. [99]For the creation of biosensors for sensing environmental contaminants, many types of nanomaterials such as quantum dots, and metallic and carbonaceous nanoparticles have been employed. According to Zhou et al. (2019), nano-porous materials such as metal/metal oxide provide a viable platform for the creation of sensors that can detect contaminants in polluted samples rapidly and efficiently [100]. Nano porous metal oxide-based gas sensors have been created to investigate environmental contaminants emitted by agricultural and medical sectors. Pollutants in water, food, and farmland have been identified using nano-based technologies such as biosensors.

5.1. Remediation of pollutants in water

Various studies have investigated the manipulation and formation of biopolymers by the diverse microbial species discovered during wastewater treatment [100],[101] in a slow process because of the inherent complexity of the systems involved. Removal of heavy metals or various other impurities is necessary [102] which is accomplished by various polymers (nanocellulose, graphene oxide, etc.) and some basic oxides (Fe_2O_4, Al_2O_3, ZrO_2, etc.).[103][104] The removal of fluorides and chlorophenols involves some of the polymers deploying processes like adsorption, precipitation, electrolysis, and membrane separation.[105][106] In addition, inexpensive adsorbing materials are being explored like spent bleaching earth, kaolinitic clay, agricultural by-products, and biogas residual slurry for use in the defluorination of water.[107]

a) Nanocellulose

In general, nanocellulose-based materials are in high demand because of their versatility, large surface area, and renewable nature and can be broadly divided into two categories namely monocrystalline cellulose (MCC) and nanofibrillated cellulose (NFC).[108] Due to the presence of the amorphous and crystalline nature of NFC, at low concentrations (below 1 weight %), their long fibrils entangle and produce highly viscous suspensions.[109] One unit of nanocellulose polymer has the formula $(C_6H_{12}O_5)_n$ and its structure is mentioned in **Fig. 7**. All these properties contribute to the removal of F^- and other such contaminations from water with appropriate modifications **(Fig. 8)**.

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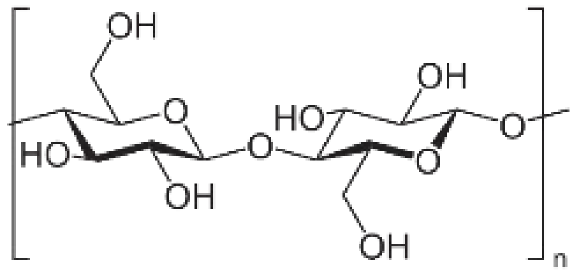

Fig. 7: Structure of a unit of nanocellulose.

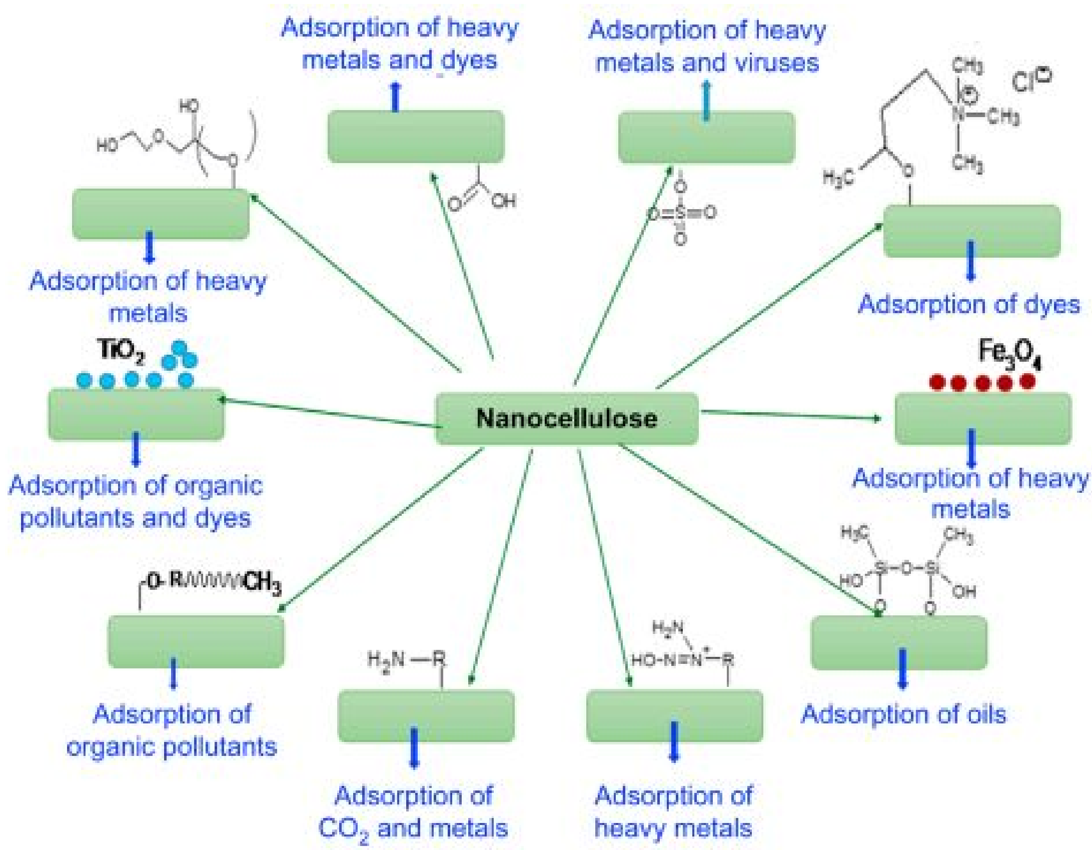

Fig. 8: Possible strategies for surface modification of nanocellulose according to the pollutant class.[110] Reprinted with permission from Woodhead Publishing Series (2017)

b) Nanochitin

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After cellulose, chitin is the biopolymer that is most widely available owing to its ideal properties like its nontoxic, biodegradable, and renewable nature. Electrostatic action and filling are two important aspects of nanochitin. When chitin functions as an emulsifier and a saltiness-enhancing agent, electrostatic action is expressed. Because of their positive charge, nanofibers can absorb negatively charged particles like oil droplets, which decreases the digestion of lipids, increases the release of sodium, and increases the bioavailability of fat-soluble vitamins. A double layer of chloride is adsorbed on the surface of chitin nanofibers in response to static electricity, increasing the amount of free sodium and enhancing the salty flavour. Nanochitin can be added as a filler to certain composite membranes, such as those based on starch or gelatin, to enhance their antifungal, thermal, and physical characteristics. Additionally, chemical derivatization or post-functionalization can be used to chemically modify and functionalize a significant amount of hydroxyl and acetamide groups that are exposed on the surface of nanochitin. By filling in gaps and creating winding pathways between water molecules, nanochitin can enhance the gelatin film's ability to withstand water vapour. F-SiO_2 can aid in the composite membrane's development of a superhydrophobic surface. Biomimetics enables the development of composite materials containing iron and silica to produce specific functionalities (both nutritional and physical).[111]

c) Graphene Oxide (GO)

A mono-layer carbon sheet that is held together by a hexagonal honeycomb lattice is known as graphene. According to the Hummers method, graphite can be oxidized with a strong oxidant and then exfoliated to produce graphene oxide (GO).[112] Due to its thickness and various other unique properties, GO is used for the purification of water and can be further changed, creating hybrid nanocomposites using additional nanoparticles, suitable for multicomponent pollutant removal such as cationic, anionic, and amphiphilic pollutants;[113] GO enhances the removal effectiveness and reusability of other materials. Besides graphite, GO can also be produced using some biological and natural resources such as coal, lignocellulose, cellulose, among others. For wastewater treatment, both single-walled and multi-walled GO are used.[114]

5.1.1. Removal of heavy metals

Heavy metal contamination of water supplies is a major issue that affects the environment as these metals enter aquatic ecosystems directly through industrial effluent discharge, leaching of heavy

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metal-contaminated soil, refineries, etc. The contaminating heavy metals comprise Cu^{2+}, Cd^{2+}, As^{5+}, Pb^{2+}, Hg^{2+}, Cr^{6+}, Mn^{2+}, Zn^{2+}, and Ni^{2+}.[115][116][117] All these pose a very serious threat to human health for example Hg^{2+} causes severe damage to nervous systems, Cu^{2+} causes liver and kidney damage, etc. Thus, the removal of heavy metals is absolutely necessary from the polluted water[115][118][8]

Table 4 lists a number of studies that have deployed polymer-based nanocomposites to remove heavy metals from water along with their adsorption capacities towards heavy metals. Additionally, pH significantly affects how much pollutant is taken up by composites[119] as in the case of absorption of Cr^{6+} decreased with an increase in pH because the $-NH_2$ groups on the composite's surface are less protonated; at pH 2.0, the composite could absorb 171.5 mg/g of Cr^{6+} at its maximum rate. For the removal of Cr^{6+}, polypyrrole has been used which is essentially organically modified montmorillonite clay nanocomposite as the absorbent [120] wherein the amount of clay in the composite had a big impact on how well Cr^{6+} could bind in aqueous solutions.[121]

The Hg^{2+} ions have been removed from water using a composite of mesoporous silica and polyacrylamide (PAAM) where the physical adsorption of Hg^{2+} onto the composite proved a reversible process as the composite can be regenerated without losing its capacity to adsorb Hg^{2+}. [122] In the case of physical adsorption, the temperature affects the adsorption of the adsorbate negatively, and as the temperature rises, the uptake of heavy metals decreases; the highest amount of Hg^{2+} that the composite could have absorbed on an increase in temperature from 25-40 °C was reduced to 157.5 mg/g.

Table 4: Polymer composites as adsorbents for the removal of heavy metals [123]

Nanocomposites	Names of heavy metals	Maximum adsorption capacity (mg/g)
Chitosan- rectorite	Cu^{2+}, Cd^{2+}, and Ni^{2+}	13.32-Ni^{2+}
(MWCNT/PU) Multiwalled carbon nanotube-polyurethane	Pb^{2+}	270.27
Chitosan montmorillonite	Cu^{2+}	134.62

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Chitosan-clay composite with epichlorohydrin cross-linking	Cd^{2+} and Ni^{2+}	72.31-Cd^{2+} 32.36-Ni^{2+}
Chitosan montmorillonite	Co^{2+}	150
graphene oxide/chitosan	Cu^{2+}, Cr^{6+}	78.80-Cu^{2+} 32.76-Cr^{6+}
Chitosan-clay	Cu^{2+}	181.5
Magnetic cellulose with amino functional group	Cr^{6+}	171.5
Exfoliated montmorillonite modified organically with polypyrrole	Cr^{6+}	209.0
Mercapto-functionalized Fe_3O_4 nanoparticles	Hg^{2+}	256.4
Nanohydroxyapatite-alginate	Pb^{2+}	270.3
Nano-hydroxyapatite-chitosan	Cd^{2+}	122.0
Chitin/chitosan-nano-hydroxyapatite	Cu^{2+}	6.2
Alginate/Mauritanian clay	Cu^{2+}	47.6
Mesoporous silica/ polyacrylamide	Hg^{2+}	177.0
poly (vinyl alcohol) clay/ carboxymethyl chitosan	Cd^{2+}, Co^{2+}, and Cu^{2+}	2470-Cd^{2+} 385-Co^{2+} 794-Cu^{2+}
TMSPEDA hybrid polymeric nanocomposite /PMDA	Pb^{2+}, Zn^{2+}, and Cd^{2+}	49.72-Pb^{2+} 41.75-Zn^{2+} 45.22-Cd^{2+}

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5.1.2. Removal of dyes

Since the dawn of human civilization, dyes have been employed as a coloring agent and back then majority of them came from natural sources. However, today thousands of synthetic dyes in the market have nearly completely replaced the natural ones.[124]

Synthetic dyes are typically categorized into various groups such as acid dyes, direct dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, and sulphur dyes. Both acid and basic dyes are water-soluble; acid dyes have a carboxyl or sulfur-based group in their chemical structure, while the basic dyes have amino groups, which impart them a (+)ve charge up on dissolution in water.[125] Sulphur dyes and vat dyes are among the inexpensive dyes for coloring and are water-insoluble too. The reactive dyes are highly coloured organic substances that undergo hydrolysis as they are colored because their functional group is bonded to water. Water-soluble dyes include direct and dispersed dyes.[126] The chemical structures of direct dyes typically have unmetallized azo structures, while the molecular structures of dispersed dyes normally contain anthraquinone or azobenzene with one or more functional groups attached to them.[127] Some examples of polymer composites as dye-removal adsorbents are mentioned in **Table 5.** [128]

Table 5: Polymer composite adsorbents deployed in the removal of dyes [123]

Nanocomposite	**Dyes**	**Maximum adsorption capacity (mg/g)**
Montmorillonite-organocellulose acetate composites that resemble paper	Acid scarlet G	95.1
montmorillonite /chitosan-g-(*N*-vinylpyrrolidone)	Rhodamine 6G	36.6
basic Yellow 28 571.4 montmorillonite amidated pectin	Basic Yellow 28	571.4
Anionic clay and alginate that resembles hydrotalcite	Orange II	2.8 (mmol/g)

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Chitosan clay	Methylene blue	142
acrylic copolymer-bentonite and chitosan	methyl violet; malachite green	2280 for malachite green; 3057 for methyl violet;
Poly HEMA-chitosan-MWCNT	Methyl orange	416.6
carbon tubes/spherical cellulose/	hybrid Methylene blue	302.1
graphene oxide/chitosan	Methylene blue and methyl orange	508.56 for methylene blue; 245.49 for methyl orange;

Even in low quantities, the majority of synthetic colors are visible in the water, and therefore, effluent containing synthetic colors must be treated before being released into the environment. The ideal approach for treating wastewater containing colors is the adsorption procedure and assorted polymeric nanocomposites have been utilized as adsorbents **(Table 6)** even for the large-scale wastewater treatment process.[129]

5.2. Soil Remediation

The strengthening of the soil, with increased cohesion and strength, and resistance to erosion, including reduced permeability, are all desirable traits for soft soil. Improving all these soil properties is be anticipated process, in terms of environmental concerns[130] where ideal solutions are offered by biopolymers[131] The effects of applying different concentrations of biopolymer on the enhancement of soil strength have been experimentally investigated using direct shear tests and splitting tensile unconsolidated undrained triaxial; specimens treated with biopolymers demonstrated better resistance to environmental influence.[131] **Fig. 8** represents a laboratory vegetation growth experiment which shows that both, the seed germination and overall growth in cultured soil are promoted by biopolymers **(Fig. 9(a))** and natural inorganic silty loam **(Fig. 9(b))**.

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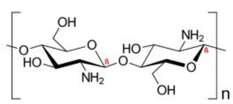
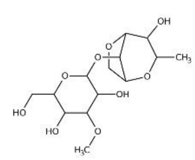
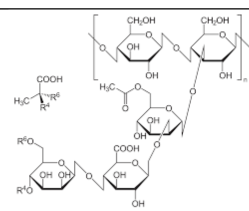
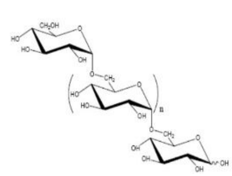
Some examples of biopolymers with their behavior toward soil remediation are presented in Table **6**.

Table 6: Biopolymers with their characteristics and uses towards soil remediation:

Serial No.	Biopolymers	Composition	Structure	Characteristics	Behaviour towards soil remediation	References
1.	Chitosan	$C_{56}H_{103}N_9O_{39}$		-Soluble in acidic solvents. -Biodegradable -Low mechanical strength. -Low-temperature response rate.	-Coagulant effects -Removal of heavy metals in water	[132] [12]
2.	Agar Gum	$C_{14}H_{24}O_9$		-Ability to form reversible gels. -Thickening agent	-Pore clogging -Erosion reduction	[12]
3.	Xanthan Gum	$C_{36}H_{58}O_{29}P_2$		-High viscous rheology	-Drilling mud thickener -Strengthening	[12]
4.	Dextran	$C_{18}H_{32}O_{16}$		-Flexible biopolymer -Emulsifier	-Drilling muds -Erosion reduction	[12]

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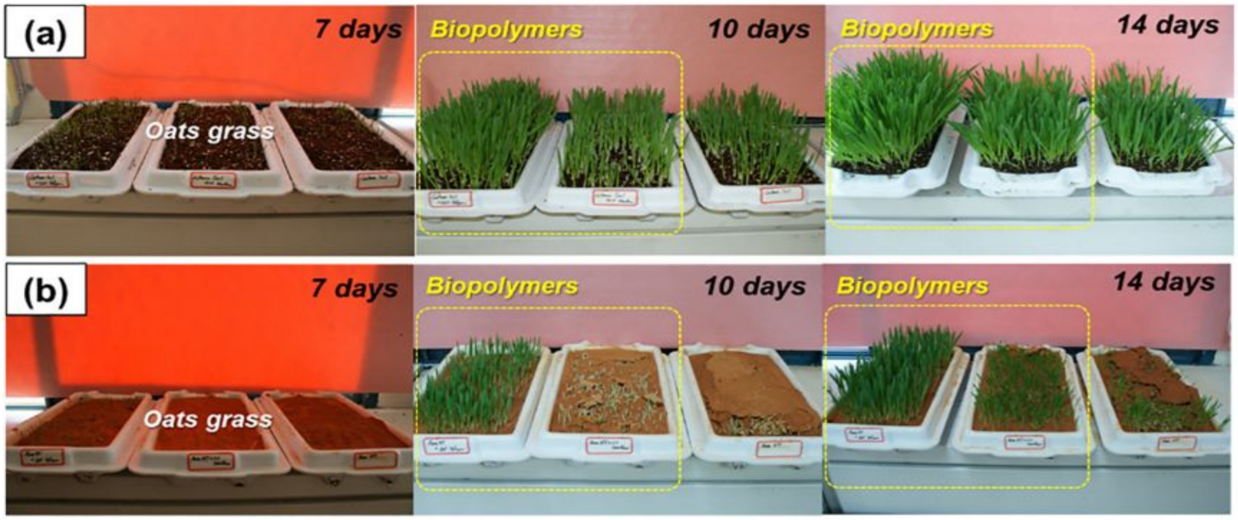

Fig. 9: Vegetation promotion effect assessed in the laboratory **(a)** Culture soil. **(b)** Inorganic silty loam.[133] Reprinted with permission from Elsevier (2020)

a) Chitosan

Chitosan is a deacylated form of chitin and NaOH treatment is usually employed to extract it. This biodegradable, biocompatible, renewable, and hydrophilic biopolymer has been deployed in a wide range of applications[134] in various fields like material science, food and nutrition, medical science, immunology, microbiology, agriculture, and wastewater treatment products.[135] Chitosan has been demonstrated to have the ability to decontaminate groundwater that contains contaminants like Cu^{2+} and P^{-} in geotechnical and geoenvironmental settings.[136] By lowering the hydraulic conducting capacity of sandy soils, chitosan-coated sand particles can produce a suitable plugging effect in filters for the treatment of polluted groundwater.[137][128]

b) Agar Gum

Agar gum is a polysaccharide from the *Rhodophyceae* family and is made up of linked galactose molecules. After being dissolved in boiling water, agar gum, due to its thermoregulation quality, enables the formation of solid gels up on cooling to room temperature. Sand's strength is effectively increased by agar gum without endangering the environment wherein results showed

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that using 3% thermally treated agar gum increased the soil's unrestricted compressive strength by up to 10 MPa up on drying.[136]

c) Xanthan Gum

Xanthan gum is a polysaccharide made by the bacteria *Xanthomonas campestris* and it exhibits hydrocolloid rheology and is used as a viscosity thickener. Through pore filling and raising the liquid limit, it has been added for the reduction of the hydraulic conductivity of silty sand and for enhancing the soil's undrained shear strength. Another recent study examined the xanthan gum's potential to strengthen the soil and demonstrated that xanthan gum preferably forms firm clayey soil matrices through hydrogen bonding.[138]

d) Dextran

It is an adaptable biopolymer that can create coils in an aqueous medium that has a low level of permeability and a high density. This polymer is one of the first industrially utilized extracellular microbial polymers, commonly used as blood plasma extenders. The significant use of dextran has been in the industrial separation of plasma proteins, especially pro-insulin, albumin, and other factors of blood. Dextran increases the surface erosion and scouring resistance of saturated silty sands, according to recent experimental research but it has no effect on soil water retention, according to a study examining its impact on the desiccation and rehydration of sand and clays. In comparison to untreated conditions, the critical shear stress (τc) and erodibility coefficient (k) of fine silica sand containing dextran increased 20 times and 1/9, respectively.[139]

5.2.1. Clogging Effect of Biopolymers and Hydro-Dependency

Dehydrated biopolymer gels or biopolymer-clay matrices tend to absorb and transmit water to hydrogels leading to volumetric expansion when soils contain a greater quantity of water. As the water content increases, the elastic properties of the biopolymers (e.g., tensile strength, stiffness) decrease exponentially, which results in a significant decrease in soil strength (roughly one-tenth of its strength in the dried state) when the soil is fully saturated.[140] However, when the soil is rewetted with a biopolymer mixture (e.g.: clay soil (200 kPa) versus sandy soil (50 kPa) in most cases), the uncompressed strength of the rewetted soil is much greater than the strength of untreated soils.[136]

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In addition, the swelling of the hydrating biopolymer material fills the pores of the soil (especially in sand) thus causing it to become more clogged, resulting in a reduction of hydraulic conductivity by more than three to four orders of magnitude. As a result, biopolymers have potential applications in hydraulic engineering, e.g., slurry walls, seepage barriers, and grouting.[141]

5.2.2. Biopolymers in Geotechnical Engineering

Biopolymers, in contrast to other ground improvement techniques, perform well in the midst of fine soils. Furthermore, they can be incorporated into the soil through a variety of practical methods, such as mixing, injecting, spraying, or grouting.[142] Additionally, they can be employed in the construction industry, as well as in the construction of earth pavement and the prevention of erosion in farmland (**Fig. 10**). They tend to form a permanent gel matrix within the soil, which does not adversely affect the local environment. In combination with their water-retaining properties in the soil, it is assumed that biopolymers may be able to stimulate vegetation growth.[143]

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Fig. 10: Schematic representation of applications of biopolymers in the field of geotechnical engineering.[136] Reprinted with permission from Sustainability (2016)

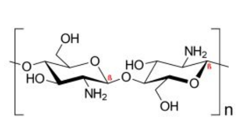
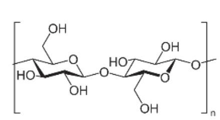
Direct biopolymer implementation has several advantages over other bio-soil approaches, but the main one is that biopolymers can be generated ex-situ and used in-situ with a higher level of quality control, whereas Microbially Induced Calcium Carbonate Precipitation (MICP) requires time-consuming in-situ cultivation. Biopolymers being economically mass-produced, can react with soil particles quickly after mixing, making them useful for temporary or urgent support.

5.3. Air Remediation

There are only a few methods and biopolymers available for the filtration of air [144] applications because of the structural complexity of these polymers which makes the process challenging and difficult.[145]

This includes the deployment of some additional techniques for producing nanofibers, like, electrospinning, template synthesis, and thermally induced phase separation. The primary capturing mechanisms identifying the pollutant preservation on the filter media are particulate matter (PM) size and physical effects, delineating the function of particulate air filters in filtration.[146]

Table 7: Biopolymers with their characteristics and behaviour towards air remediation

Serial no.	Biopolymer	Formula	Structures	Characteristics	Environmental Application	References
1.	Chitosan	$C_{56}H_{103}N_9O_{39}$		-Soluble in acidic solvents. -Biodegradable	-Agricultural bio-pesticide -Used for its antibacterial properties	[6]
2.	Cellulose	$(C_6H_{12}O_5)_n$		-Excellent mechanical properties	-Act as aerogels and hydrogels towards air filtration	[6]

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				-Hydrophilic in nature		

Inertial impaction, straining, gravitation, electrostatic attraction, diffusion, and fiber-pollutant interaction on the filter's surface are some of the filtration mechanisms that work for particles smaller than the pore size of the filter.[147] It should be emphasized that for nanofibers, interception, and diffusion mechanisms are more effective than gravitation, straining, and inertial impaction. These mechanisms are often most common for capturing particles with a diameter of 0.5 µm.[148] According to studies, interception and Brownian diffusion can cause particles with sizes between 50-500 nm to be removed by the nanofibrous media. Numerous studies have also demonstrated that nanofibers with a higher packing density and a smaller fibre diameter enhance the interception effect.[149] The strength of the diffusion mechanisms and interception is indicated by the Peclet number; a strong diffusion mechanism requires a lower Peclet number and a higher Knudsen number.[150] It is also realized that biopolymer-based nanofilters primarily use the same size-based filtration and physical mechanism. Additionally, these mechanisms support the biopolymer-based nanofilters' ability to achieve better particulate filtration efficiency, particularly for smaller, charged, or functionalized particles.[151] Some examples of biopolymers with their behaviour toward air remediation are presented in **Table-7**.

Gaseous pollutants: Gaseous pollutants can be captured through two primary capture mechanisms: physisorption (intermolecular attraction) and chemisorption (chemical action). Physisorption is the capture of gaseous pollutants through the surface pores of a fibre structure whereas more selective chemisorption entails the conversion of pollutants into simpler compounds through a chemical reaction, such as catalytic or non-catalyst reduction.[152] The higher surface area of nanofibers increases the capacity for physisorption, and hence the reason fibrous filter should be designed with a very high surface area; functionalized electro-spun nano-membranes made from various polymers may be useful for this purpose. For the measurement of gaseous pollutants, various experimental configurations are available[153] as illustrated in **Fig. 11**.

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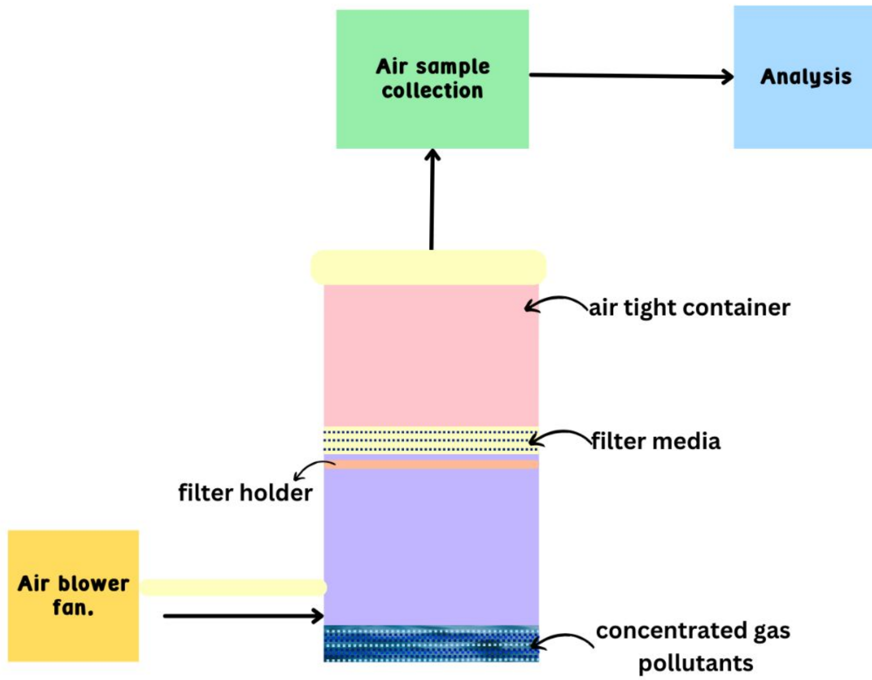

Fig. 11: Schematics of the experimental setup for characterization of gas filter

5.3.1. Antimicrobial air filters

Bioaerosols are among the dangerous pollutants that endanger humans, wherein a high-performance air filter can be deployed to trap and destroy biohazards. However, the buildup of the collected bioaerosols in the air filters poses a serious problem since, given enough moisture and nutrients, the bacteria may proliferate and spread throughout the whole filter.[154] Additionally, the particulate and chemical contaminants that are trapped in the filter may help to promote the development of bacteria, which might significantly reduce the effectiveness of filtration and eventually cause the filter to degrade (bioporation).[155] The possibility of the volatile compounds generated by microbial metabolism being discharged from broken filters to the air again is another concern with such filters. The purpose of antimicrobial air filters is to remove or kill biological contaminants from the air.[156]

Both in research labs and in real-world applications, a wide range of synthetic polymers and biopolymers with or without the addition of additives may be used to create nanofiber membranes.[153] The most popular and advanced polymers, as well as the fabrication methods, utilized to create nanofibers for filtering applications are presented in **Table 8.**

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Table 8: Most popular and cutting-edge polymers deployed to create nanofibers for filtration applications and manufacturing processes.

Polymer Materials	**Method/ Application**
• **Commonly used plastics:**	
(PP) Polypropylene	Filtration; Electric whirling melts.
(PE) Polyethylene	Filtration; Electric whirling melts.
(PVC) Poly(vinyl chloride)	Filtration; Electrospinning.
(PS) Polystyrene	Matrix for composite materials and filtering; Electrospinning.
• **Advanced and special polymers:**	
(PAN) Polyacrylonitrile	Filtration; Electrospinning; A forerunner to the production of CNF.
(PEO) Poly(ethylene oxide)	Electrospinning. Filtration; model components.
(PVA) Poly(vinyl alcohol)	Electrospinning; conductive polymer-carriers; food packaging; filtering;
(PU) Polyurethane	Electrospinning; protective gear; filtering; composite material matrix.
(PA) Polyamides	Electrospinning; strengthening; filtering; model materials.

Traditional antimicrobial agents, namely metals like Ag nanoparticles and metal oxides, which are expensive and can permanently harm both humans and the environment, have been used to treat or combine fibrous filters to achieve antimicrobial properties.[157]

Current air filters vs. traditional air filters: Presently, three primary kinds of air filters are available commercially: antimicrobial air filters (Ag particles), chemical air filters (Carbon C in its activated form), and particulate air filters (such as high-efficiency particulate air, HEPA) **(Fig. 12)**. Air filters comprise porous materials like fibrous non-woven mats with micro-sized fibres

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arranged in a random pattern. The fibres are created using chemically created polymers based on petroleum.[158]

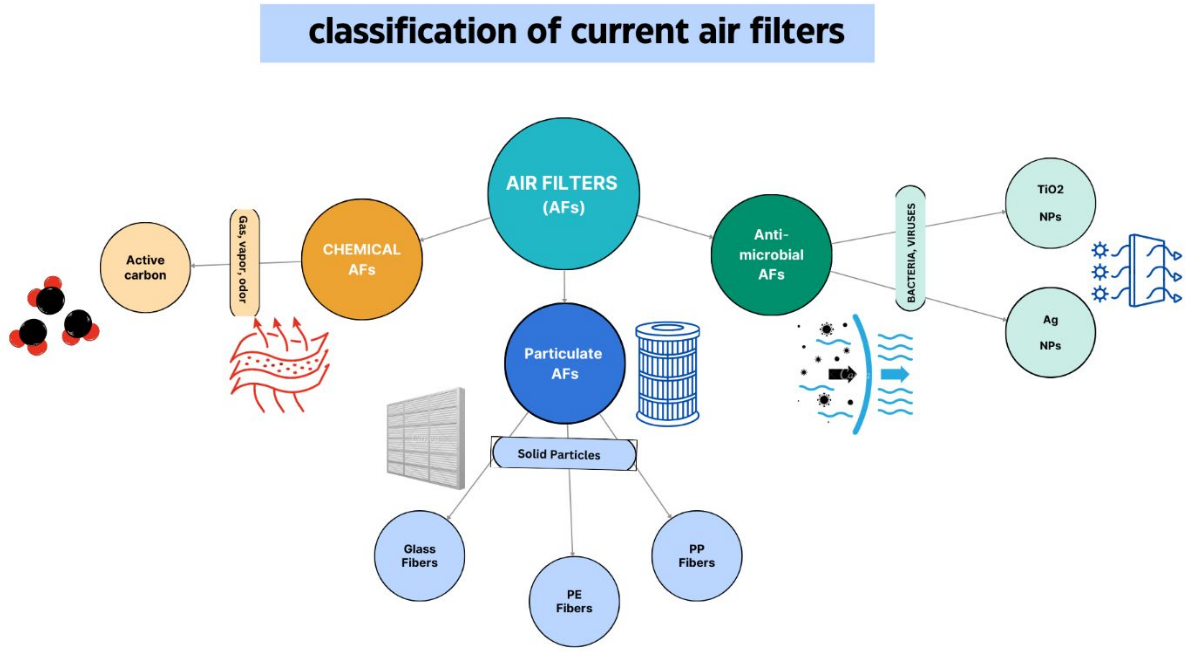

Fig. 12: Classification and types of the air filters that are currently deployed.

Large concentrations of expensive nanoparticles, such as Ag or TiO_2, that have antibacterial properties, are frequently found in antimicrobial air filters. However, it has been shown that both chemical filters and PM provide poor protection against risks. Therefore, in modern air filtration systems, a variety of filters may be used to achieve high-quality air, including regular particulate filter, HEPA filter, activated carbon filter, and antimicrobial filter, among others.[159] As is to be expected in such systems, there is a significant pressure drop downstream from the filters, resulting in the additional cost of active air exchange filtration and the rise in energy consumption. There are a number of challenges associated with the current air filter materials that are being studied and are worth discussing.[160] Firstly, in addition to cellulose-based filters, none of the conventional polymeric materials used, such as PP and PE, various additives, and glass fiber are environmentally friendly; they cannot be disposed of easily. Secondly, existing air filters may not be able to filter out a wide range of pollutants due to insufficient interactions with the filter materials.[161] Thirdly, additional additives loaded into or on the filter mats, such as activated

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carbon and nanoparticles, may lessen the filter's effectiveness and increase the amount of active air exchange fuel used.[162]

The fabrication of air filtering materials is a complex and costly process, particularly for those that require the use of selected catalysts or nanoparticles. Furthermore, the filtration process in most common filters is decided by mechanisms based on size and physical properties, which are only effective for the capture of particulate matter.[163] These mechanisms are not suitable for the elimination of toxic gas molecules or antimicrobial filtration.[164] Consequently, the creation of bio-based multifunctional air filtering materials with high removal efficiencies ought to be affordable for various types of pollutants (such as particulate matter, toxic gases, and biological hazards) while also maintaining low airflow resistance, a challenging task for the development of advanced bio-based materials for air filtration systems.[165]

Air Mask Filter: An appealing substitute for filter materials that may be able to solve the aforementioned issues is offered by biopolymers, being widely accessible, frequently inexpensive, and easily processed. They mostly include polysaccharides and proteins derived from both plant and animal sources, such as cotton cellulose, animal wool, silkworm silk, and soy and corn proteins **(Fig. 13)**.[151] Biopolymers possess chemical and physical characteristics that are crucial for the elimination and absorption of particular chemical pollutants or offer viricidal or bactericidal action that can be helpful in filter applications.

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Fig. 13: Materials for biopolymer-based filtration made from various protein and polysaccharide sources. Particulate matter (PM), viruses, bacteria, and smoke pollutants can all be filtered out due to these particular surface chemistries and varied molecular interactions.[151] Reprinted with permission from ACS Publication (2021)

There are two main categories of air filtering methods. Through a process known as physical adsorption, the harmful pollutants initially cling to the embedded particle or filter surface on the filter. The other is chemisorption, where the pollutant interacts with either the surface of the filter membrane or a particle that is embedded in it to produce an inert product.[166] The accessibility of the active sites inside the filter is the limiting element in both situations. In other words, the leftover toxins may still pass through the porosity filter when there are no longer any active sites for them to bind. **Fig. 14** deliberates the earlier air filters that used synthetic polymers to filter particles based on interception, impaction, electrostatic interaction, and diffusion.

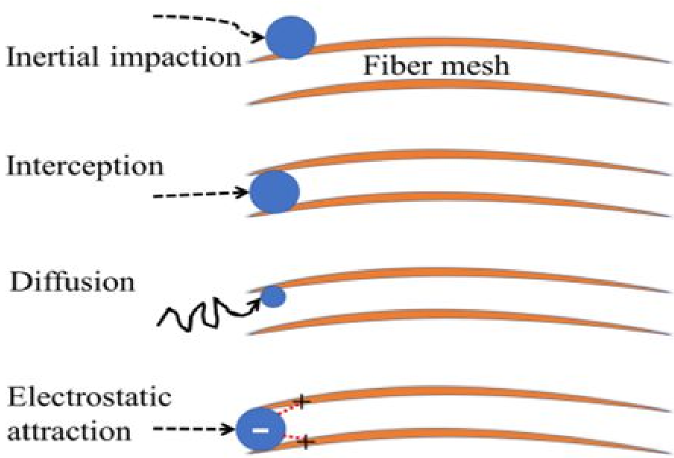

Fig. 14: Impaction, diffusion, interception, and electrostatic interaction are frequently used filtration mechanisms for biopolymer (orange lines). The pollutant, represented as a blue sphere, moves along a black path, and interactions between the pollutant and the biopolymer are shown as red dotted lines. [151]

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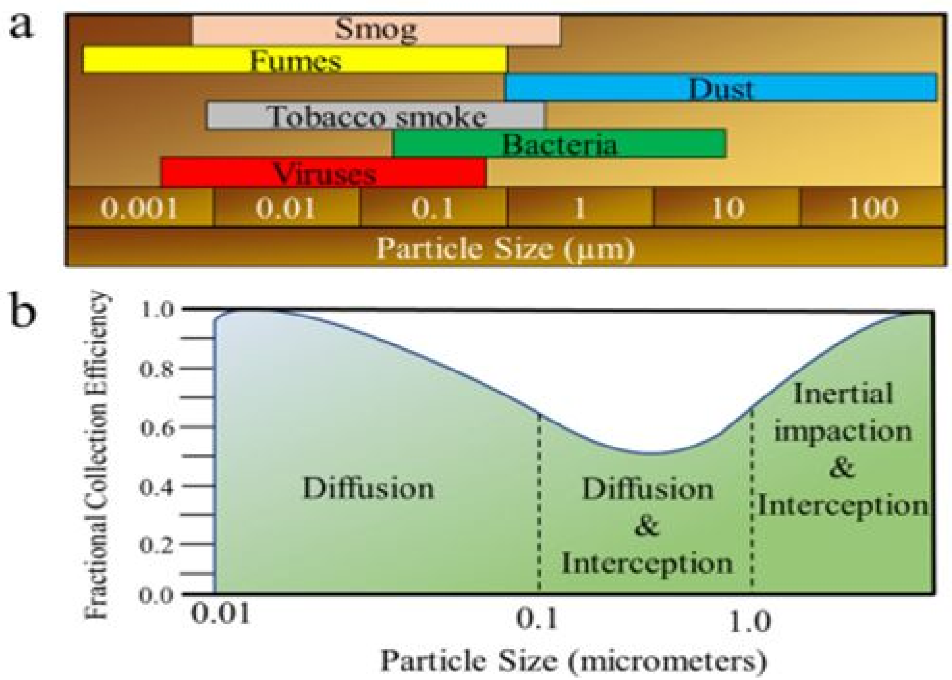

Fig. 15: **(a)** Size proportions of common air pollutants; and **(b)** fractional collection effectiveness for various mechanical filters in relation to contaminant diameter [151]

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The interactions also hold true for biopolymer-filters based on biopolymers. The type of the pollutant and its size are the major factors affecting the filtration interaction. (**Fig. 15(a)**), whereas big-sized pollutants (>1000 nm) may be easily stopped, smaller pollutants are largely filtered through biological processes. (**Fig. 15(b)**) reflects the fractional collection effectiveness of various mechanical filters in relation to the contaminant's diameter.[167]

6. Conclusion and future prospects

The integration of greener nano biopolymers into environmental cleanup represents a significant advancement towards achieving sustainability in addressing pollution. As the environmental challenges grow in scale and complexity, the deployment of these innovative materials has delivered promising results in remediating contaminated sites, removing pollutants from water, and mitigating the release of toxic substances into the ecosystem. [168]

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In conclusion, greener nano biopolymers offer a unique combination of biodegradability, renewability, and effectiveness in environmental cleanup processes. Their ability to be engineered at the nanoscale enhances their surface area, reactivity, and specificity toward targeted pollutants, making them superior to traditional remediation materials. Additionally, the use of biopolymers derived from natural resources aligns with the global push towards reducing carbon footprints and promoting circular economy practices. [169]

However, the journey toward widespread adoption of these materials is still in its early stages. Future research should focus on scaling up production processes, reducing costs, and improving the functionalization of these materials to target a broader range of pollutants. Moreover, the long-term environmental impact of deploying nano biopolymers at a large scale remains a critical area of investigation. While these materials are designed to be eco-friendly, their interactions with different ecosystems, particularly in the case of nanoscale materials, need to be thoroughly assessed.

Future prospects in this field also include the development of hybrid materials that combine the properties of nano biopolymers with other sustainable technologies, such as bio-based catalysts and green energy sources, to enhance their effectiveness and applicability. The integration of smart technologies, such as sensors and responsive materials, could also pave the way for more efficient and autonomous environmental remediation systems.

Furthermore, the detection and quantification of toxic matter in the environment can be significantly improved through the use of nano biopolymers, offering more sensitive, selective, and rapid monitoring tools. [170] This would not only facilitate the early detection of pollutants but also enable more precise interventions, thereby minimizing the environmental impact. [171]

The potential for greener nano biopolymers to revolutionize environmental cleanup is immense, but it requires a concerted effort from the scientific community, industry stakeholders, and policymakers to fully realize their benefits. [172] By fostering interdisciplinary collaborations and promoting sustainable innovation, the future of environmental remediation looks promising with greener nano biopolymers at the forefront. [173]

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Conflict of interest: Authors declare no conflict of interest

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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Abbreviations:

BNC: Bacterial Nanocellulose

CNC : Cellulose Nanocrystals

CNF: Cellulose Nanofibers

CNW: Cellulose Nano whiskers

FTIR : Fourier Transform Infrared

GO : Graphene Oxide

MCC : Microcrystalline Cellulose

NFC : Nanofibrillated cellulose

NP : Nanoparticles

OH : Hydroxyl

PCL : Polycaprolactone

PCM : Polychlorinated biphenyls

PLA : Polylactic Acid

PVA : Polyvinyl Alcohol

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SEB : Steam-exploded bamboo

SEN : Single enzyme nanoparticles

SF : Silk Fibroin

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Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.