

Review

Microbial Biopolymers: From Production to Environmental Applications—A Review

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Abstract: Industrial evolution and agricultural expansion, explained by continuing population growth, have rendered enormous problems for the world throughout the past few decades, primarily because of waste generation. To reduce environmental impact and dependence on fossil fuels, scientists have explored replacing synthetic polymers with environmentally friendly and sustainable alternatives in many emergent applications. In this regard, microbial biopolymers have gained special attention. Many biopolymers originating from various strains of bacteria, fungi, and algae have been reported and their possible applications have increased rapidly. This review focuses on the wide range of microbial biopolymers, their characteristics, and factors influencing their production. The present study also describes the environmental applications of microbial biopolymers. The use of these biopolymers is very attractive as a value-added and sustainable approach to wastewater treatment. By acting as adsorbents, coagulants, and flocculants as well as filters in membrane processes, microbial biopolymers shine as promising solutions beyond conventional methods. They can be integrated into various stages of the treatment process, further enhancing the efficiency of wastewater treatment methods. Microbial biopolymer applications in bioremediation and soil stabilization are also reviewed. Several studies have demonstrated the strong potential of biopolymers in soil improvement due to their ability to minimize permeability, eliminate heavy metals, stabilize soil, and limit erosion. Challenges related to scaling up and the downstream processing of microbial biopolymers, as well as its future perspectives in environmental applications, are also discussed.



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1. Introduction

The worldwide population is consistently expanding, necessitating the expansion of the food supply and putting pressure on the limited available natural resources. This shift has ushered the agricultural sector into forming a noteworthy amount of waste. The environment is frequently being polluted due to rapid industrialization and the shift of populations to urban areas, leading to several concerns such as water pollution, waste expulsion in the surroundings, and environmental deprivation [1,2].

Faced with this significant increase in the global population, modern agriculture is proving to be an advantageous solution since it offers the opportunity to upsurge crop yield. However, it also led to an increase in the global carbon footprint, and the generation of waste from farming impacts the economic and social sectors. As per [3], agriculture comprises around 38% of the terrestrial surface area on Earth. The Food and Agricultural Organization (FAO) stated that the amount of food wasted annually during farming, post-harvesting, and agriculture processing was 1.3 billion tons [4]. The utilization of agricultural residues and their transformation into biopolymers presents a great opportunity to reduce the global carbon footprint, considering that the landfilling of residue promotes global warming.

The increasing concern for diverse environmental problems has led to the development of new approaches to diminish its deteriorated effects. Amidst various approaches,

the formation of microbial biopolymers is a method that has earned great engagement due to its superiority over synthetic biopolymers in terms of sustainability, biodegradability, cost-effectiveness, structural diversity, non-toxicity nature, and bioactivity. This is due to a customized range of functional groups with defined molecular weights. Biodegradability relies on its chemical network so that it can be debased by biological attack. Moreover, the approach to the degradation of biopolymers relies on factors such as dampness, temperature, and pH. However, various functional, thermal, morphological, and rheological tests are usually executed to check its capability [5].

Nowadays, many synthetic polymers are more admissible and have become a regular part of our lives, including dyes, Teflon, plastic polyester, etc. Biopolymers are described as a considerable group of molecules separated from their cell walls and based on repeated functional units at a specific level. Microbes are cell-forming manufactories that can transform carbon and nitrogen into extensive amounts of extracellular, intracellular, and capsular biopolymers. Based on chemical configurations, microbial biopolymers are classified into polyphosphates, nucleotides, polysaccharides, polyamides, and polyesters. Among all polyesters, biopolymers are widely adequate and are manufactured through metabolic pathways [6]. Some microbial biopolymers have drawbacks such as poor functional and mechanical attributes and sensitivity towards chemicals; these can be mitigated by developing hybrids or nanobiocomposites using nanofillers.

Many researchers have recently concentrated on the utilization of biopolymers and their potential as biomaterials. Microbial biopolymers have applications in the food, textile, agriculture, and pharmaceutical industries due to their unique characteristics. Environmental applications of microbial biopolymers have grown in popularity during the last decade. Biopolymers could be generated in large quantities for cutting-edge applications such as biofilm matrices, bio-flocculants, heavy metal adsorption, bioremediation, etc. [7–10]. This review focuses on microbial biopolymers, their classifications and characteristics, the factors influencing their production, and their emerging environmental applications.

2. Microbial Polymers

Based on origin, microbial biopolymers are categorized into three categories: (i) From bacteria, (ii) From fungi, and (iii) From algae. Bacteria are capable of producing both intracellular and extracellular biopolymers. In bacterial metabolic synthesis, polysaccharides, polyamides, polyesters, and polyphosphates are originated as metabolites [11,12]. Biopolymers produced from different bacterial strains are represented in Table 1.

Table 1. Fabrication of biopolymers from Bacteria.

Biopolymer	Category	Bacterial Strain	References
Alginate	Polysaccharide	<i>Laminaria digitata</i> spp., <i>Macrocystis pyrifera</i>	[13]
		<i>Pseudomonas</i> spp.	[14]
		<i>Komagataeibacter saccharivorans</i>	[15]
Bacterial Cellulose	Polysaccharide	<i>Komagataeibacter</i> spp. FXV3, <i>Komagataeibacter</i> spp. NFXK3, and <i>K. intermedius</i> LMG 18909	[16]
β -glucan	Polysaccharide	<i>Bacillus subtilis</i>	[17]
		<i>Xanthomonas campestris</i> , <i>Bacillus natto</i>	[18]
Hyaluronic acid	Polysaccharide	<i>Mytilus galloprovincialis</i>	[19]
		<i>Streptococcus zooepidemicus</i>	[20]
Polyhydroxyalkanoates	Polyester	<i>Bacillus megaterium</i> OUAT 016	[21]
		<i>Bacillus cereus</i> RBL6 and <i>Pseudomonas pseudoalcaligenes</i> RBL7	[22]
Poly (γ -glutamic acid)	Polyamide	<i>B. megaterium</i> WH320	[23]
		<i>B. licheniformis</i> 9945a and <i>B. subtilis</i> natto	[24]
Xanthan gum	Polysaccharide	<i>Xanthomonas campestris</i> bacterium	[25]
		<i>Xanthomonas campestris</i> WXLB-006	[26]

Biopolymers produced from both fungi and algae are represented in Tables 2 and 3.

Table 2. Fabrication of biopolymers from Fungi.

Biopolymer	Category	Fungal Strain	References
β -glucan	Polysaccharide	<i>Aureobasidium pullulans</i> ATCC 15233	[27]
		<i>Aureobasidium pullulans</i> MTCC 1991	[28]
		<i>Aureobasidium pullulans</i> HIT-LCY3	[29]
		<i>Aureobasidium pullulans</i> ATCC 15233	[30]
		<i>Saccharomyces cerevisiae</i>	[31]
		<i>Lasiodiplodia theobromae</i> CCT 3966	[32]
		<i>Aureobasidium thailandense</i> NRRL 58543	[33]
		<i>Saccharomyces cerevisiae</i> , <i>Aspergillus oryzae</i>	[18]
		<i>Rhizopus stolonifera</i>	[34]
		Mucorales	[35]
		<i>Rocella montagnei</i> .	[36]
		<i>Absidia coerulea</i> and <i>Gongronella butleri</i>	[37]

Table 3. Fabrication of biopolymers from Algae.

Biopolymer	Category	Algae Species	References
Alginate	Polysaccharide	<i>Sargassum cristaeifolium</i>	[38]
		<i>Nizimuddiniana zanardini</i>	[39]
Polyhydroxyalkanoates	Polyester	<i>Synechococcus subsalsus</i>	[40]
		<i>Chlorella minutissima</i>	[40]
		<i>Spirulina</i> spp.	[41]
		<i>Stigeoclonium</i> spp. B23	[42]
		<i>Chlorella fusca</i>	[43]
		<i>Chlorella</i> spp.	[44]
Polylactide	Polyester	<i>Microcystis</i> spp.	[45]
		<i>Corallina elongata</i>	[46]
		<i>Scenedesmus abundans</i>	[47]

The array of biopolymers that fungi effectively create possesses a characteristic of numerous interests, which renders them beneficial assets for broad-spectrum environmental applications, including as biosurfactant agents [48] and in soil carbon sequestration [49], enzyme immobilization [50], the biosorption of heavy metals, and soil emendation [51]. Algae are photosynthetic microbes that can be grown on wastewater and are not only reliant upon pure water. Among all biopolymers, polysaccharides and polyesters have significant importance from an environmental perspective. A general overview of the production of several microbial biopolymer studies through fermentation is provided in Table 4. It illustrates the microbial biopolymers synthesized from various carbon and nitrogen sources, the nutrients used in fermentation, and the yields produced under ideal fermentation conditions, as well as emerging environmental applications. In the subsequent segment, significant microbial biopolymers and their environmental applications are reviewed.

Table 4. Overview of the production of microbial biopolymers by fermentation and its environmental applications.

Biopolymer	Microbial Strains	Carbon /Nitrogen Source	Nutrient Used	Duration of Fermentation	Type of Fermentation	Fermentation Conditions (Temperature, pH, etc.)	Maximum Yield (g/L)	Environmental Application	References
Polyhydroxybutyrate	<i>Bacillus subtilis</i> NG05	Sugarcane Molasses (Maltose)	Beef extract, Peptone	18 h	Batch	pH = 7, 30 °C	4.94	Waste utilization and development of Bioplastic	[52]
	<i>Ralstonia eutropha</i> ATCC 17,699	Glycerol	NaH ₂ PO ₄ , (NH ₄) ₂ SO ₄ , MgSO ₄ ·7H ₂ O, K ₂ HPO ₄	62 h	Fed-batch	pH = 10, 60 °C	68	Potential as biodegradable material	[53]
Chitosan	<i>Penicillium citrinum</i>	Rice Straw	Potato dextrose	10 days	Solid State	pH = 6.5–7.5, 30 °C	7	Heavy metal removal	[54]
	<i>Rhizopus oryzae</i> , <i>Mucor</i> sp. (MTCC 3340), <i>Absidia coerulea</i> (MTCC 1335)	Tannery fleshing waste	Yeast extract	70 h 140 h 200 h	Submerged	pH = 8.5, 25 °C	1.53 2.74 2.05	Utilization of leather flesh waste	[55]
	<i>Gluconacetobacter xylinus</i>	Glucose	Yeast extract, Peptone	10 days	Static	pH = 5; 30 °C	-	Detection of <i>Staphylococcus aureus</i>	[56]
	<i>Gluconacetobacter</i> sp.	Apple waste	2% Fructose	7 days	Static	pH = 6.4; 28 °C	-	Removal of chromium ions	[57]
Hyaluronic Acid	<i>Gluconacetobacter xylinus</i>	Orange peel	Yeast/Peptone extract	8 days	Static	pH = 4.75; 30 °C	6.13	Waste reduction	[58]
	<i>Streptococcus zooepidemicus</i>	Cheese whey	Yeast extract	2 days	Batch	pH = 6.7; 37 °C	3.37	70 % cost reduction as compared to synthetic media	[59]
Xanthan Gum	<i>Xanthomonas campestris</i>	Wastewater, Malt	Yeast broth	72 h	Batch	pH = 7; 28 °C	15.56	Improved oil recovery	[60]
	<i>Xanthomonas campestris</i>	Wastewater, Malt	Yeast broth	120 h	Batch	pH = 7; 28 °C	-	Enhanced oil recovery	[61]
β-glucan	<i>Lasiodiplodia theobromae</i> CCT 3966	Sugarcane straw	Yeast extract, malt extract, peptone	72 h	Batch	pH = 7; 30 °C	3.28	Waste utilization: conversion of cellulose to glucose	[32]
	<i>Xylaria</i> sp. BCC 1067	Glucose	Malt extract, peptone	28 days	Batch	pH = 7; 25 °C	0.115	Antifungal activity	[62]
Alginate	<i>Azotobacter vinelandii</i>	Sucrose	K ₂ HPO ₄ ·3H ₂ O, CaSO ₄ ·2H ₂ O, NaCl, MgSO ₄ ·7H ₂ O, Na ₂ MoO ₄ ·2H ₂ O, FeSO ₄ ·7H ₂ O	20 h	Batch	pH = 7; 30 °C	3.06	Nitrogen fixation	[63]
	<i>Azotobacter vinelandii</i> ATCC 9046	Sugar beet molasses/maltose/starch	Yeast extract,	72 h	Batch	pH = 7.2; 30 °C	5.44	Adsorbent for heavy metals	[64]
γ-PGA	<i>Bacillus subtilis</i>	Sago and Soyabean	Yeast Extract	5 days	Batch	pH = 6.5; 37 °C	35.32	Act as a Bio flocculant	[65]
	<i>Bacillus subtilis</i>	Glucose	Beef extract, Yeast extract, Peptone	2 days	Batch	pH = 7, 37 °C	25.38	Act as a Bio flocculant	[66]
Pullulan	<i>Aureobasidium pullulans</i>	Potato starch	Yeast extract, peptone	5 days	Batch	pH = 6; 26 °C	23.47	Could be used as a potential purifying agent and as a flocculant for heavy metal reduction	[29]
	<i>Aureobasidium pullulans</i>	Sucrose	Barley malt extract	170 h	Batch	pH = 6; 26 °C	50	Biosorbent of heavy metals; Protective agent	[67,68]
Polylactide	Indigenous microorganism	Mango Peel Waste	-	6 days	Anaerobic submerged	pH = 10, 35 °C	17.48	Cost-effective biodegradable material	[69]
	<i>Lactobacillus delbrueckii</i>	Broken rice	Yeast Extract, Peptone	50 h	Solid State	pH = 6, 40 °C	79	Cost-effective Biodegradable material	[70]

2.1. Bacterial Cellulose

Waste, including agricultural residue, food waste, and industrial leftovers, can give bacteria the nutrients and habitat they need to create bacterial cellulose. Examples of raw materials used for obtaining bacterial cellulose are by-product streams from sugarcane baggery waste [71] waste streams from biodiesel and confectionery industries [72], oat hull [73], rice bark [74], corn stalk [75], fruit juices [76], Nylon 6-6 hydrolysate [77], cotton-based textile waste [78], the wastewater of fermentation industries [79], etc. Bacterial cellulose is chiefly isolated by both Gram-positive bacteria and Gram-negative bacteria such as *Komagataeibacter* spp., *Acetobacter* spp., *Sarcina ventriculi*, *Pseudomonas* spp., etc. [15,80,81]. In comparison to plant-derived cellulose, cellulose produced by bacteria offers a range of amenities, which include high levels of purity, superior mechanical and thermal attributes, long-term sustainability, better water- and oil-holding capacities, high surface areas, and biodegradable attributes [82,83]. Bacterial cellulose is a linear-chain polysaccharide made up of repeating glucose monomeric units linked by β (1-4) linkages. It has a complex structural arrangement with ample hydroxyl groups and robust intermolecular interactions that hamper it from dissolving in water. It is remarkably resistant to decomposing in water because it establishes an interconnected system of linked strands of cellulose, which are bound jointly by bonds of hydrogen [84]. There are some challenges involved in scaling up bacterial-cellulose production by fermentation. Agitated fermentation and static fermentation are both viable methods for producing Bacterial cellulose. Zhong [85] investigated that bacterial cellulose produced by static fermentation is a more laborious and lengthy process than agitated fermentation, also static fermentation provides poor yield as compared to agitated fermentation. Zhong [85] also concluded that due to the high cost of bacterial-cellulose production, its application is limited as compared to plant-based cellulose. Consequently, novel affordable nutrient sources such as fermentation effluent, sugarcane molasses, and waste from fruits could additionally be utilized for the bacterial-cellulose upscaling manufacturing process. The manufacturing process of bacterial cellulose and its commercial usage has been constrained by high production costs as well as low yield. Bacterial cellulose-producing bacteria have no capacity to co-produce additional compounds with cellulose, such as lignin, pectin, and hemicellulose. Bacterial cellulose has a significant purity advantage over cellulose generated from plants. Furthermore, bacterial cellulose is biocompatible since complementary polymers and other contaminants are absent from it [86]. Due to its biocompatibility and biodegradability, it offers wide applications. Galdino et al. [87] developed a filter based on bacterial cellulose for the elimination of oil from wastewater. Their findings suggested that bacterial cellulose could be used as an alternative material for oil filter development. Cazón et al. [88], Cielecka et al. [89], and Chiaoprakobkij et al. [90] utilized bacterial cellulose as a biomaterial to improve the ductility, tensile strength, biocompatibility of composites. Similarly, Alves et al. [91] made filter membranes from bacterial cellulose for industrial water treatment. Based on bacterial cellulose, various potential biosensors have been developed for multifarious applications [92]. Some were developed for the detection of bacteria and viruses [56,93], antibiotics [94], heavy metals [57,95], dyes [96], and pollutants [97]. Moreover, many researchers have investigated bacterial cellulose-based hydrogels for the removal of heavy metals and dyes [98–100].

2.2. Microbial Hyaluronic Acid

A recurring mixture of D-glucuronic acid and D-N-acetyl glucosamine connected by β (1-3) and β (1-4) linkages, respectively, makes up hyaluronic acid, also known as hyaluronan [101]. It can be isolated from animal tissues like roosters' crest, cartilage, vitreous humor, and umbilical cords through a microbial fermentation process with the help of bacterial and yeast strains such as *Streptococcus* spp., *Mytilus galloprovincialis*, *Pichia pastoris*, and *Pseudomonas* spp. [19,20,102,103]. The D-glucuronic acid and N-acetyl glucosamine moieties of hyaluronic acid are generated from glucose-6-phosphate and fructose-6-phosphate, correspondingly, by two different pathways [104]. The molecular makeup of the hyaluronic

acid molecule reveals that it has several hydroxyl and carboxyl groups, which can result in a great deal of intramolecular and intermolecular hydrogen bonding in solutions. These bindings contribute to overall stiffness and exhibit gel-formation abilities [105,106]. Nevertheless, the advancement of microbial means of extraction has been prompted due to the obstacles in managing tissues from animals, excessive expenses, and moral complications related to hyaluronic acid generated from animals. Hyaluronic acid is the least explored biopolymer for environmental applications. The main challenge involved in microbial hyaluronic acid production is its low yield because of the extremely viscous nature of the broth, which makes it challenging to regulate the mixture and rapid transfer of oxygen. There is fierce competition for the same precursor molecules that are essential for cellular growth and the generation of hyaluronic acid. In addition, the build-up of lactic acid—the main metabolic waste product in hyaluronic acid fermentation activities—has a significant negative effect on both cellular development and hyaluronic acid production. Different approaches to prevail over these challenges include the systematic screening of proficient strains, optimization of tailored culture media, and development of sophisticated cultivation procedures [107–110]. Zhang et al. [111] recently developed a hybrid hydrogel for plant growth regulation and the adsorption of heavy metal ions. Taşdelen et al. [112] developed a composite hydrogel to remove manganese in wastewater. When it comes to fish waste (head, skin, fin) specifically, animal waste poses a serious environmental risk because almost 50% of the tissue is thrown away. It is essential to pursue initiatives related to research and development aimed at developing novel approaches that make it easier to obtain this biomaterial while also minimizing difficulties with waste management, emphasizing the significance of those initiatives. Refs. [113,114] extracted hyaluronic acid from *Scylliorhinus canicula* discards with the help of *Streptococcus zooepidemicus* strains. They concluded that among all approaches, fed-batch operatory was valuable in achieving a high yield and was beneficial in reducing the overall cost of production. Amado et al. [115] extracted microbial hyaluronic acid from agro-industrial by-products. They obtained a maximum yield of 3.48 g/L hyaluronic acid among three culture media. Moreover, hyaluronic acid has potential application as a nanofiber due to its water-resistant characteristics. Um et al. [116] and Wang et al. [117] constructed a water-resistant nanofiber with an electrospinning and electro-blowing technique.

2.3. Xanthan Gum

The commercially grown *Xanthomonas campestris* bacteria secretes xanthan gum, an exopolysaccharide [118]. It is a high molecular weight microbial biopolymer that belongs to the heteropolysaccharide category. Primarily, the carbon supply for the production of xanthan gum comes from the substrate's glucose and sucrose. Xanthan gum is constituted of a mixture of glucuronic acid, mannose, and glucose units of repetition adjoined by β (1-4) linkages. It is generally obtained by an aerobic fermentation approach accompanied by precipitation in isopropyl alcohol. The kind of fermenter employed, the way it is used (batch or continuous), the culture medium, and the growth parameters, such as the pH level, temperature, and oxygen in the medium, all affect the synthesis of xanthan [119]. It readily dissolves in cold water and displays strong pseudoplastic flow characteristics [120]. Its structural arrangement is extremely branched and complex. It is one of the most promising and commercialized biopolymers that has been used for the entrapment of living cells [121]. Because of its structural divergence and rheological characteristics, it can be employed for a variety of applications. Sulaiman et al. [122], Liu et al. [123], and Feng et al. [124] investigated the application of xanthan gum for soil stabilization and to improve soil water-retention efficacy. Ramos de Souza et al. [125] and Keykhosravi et al. [126] employed xanthan gum to boost oil recovery. Oil recovery was improved due to wettability modification, and increased water viscosity was achieved using a nano-polymer suspension. The findings of Ko et al. [127], Njuguna and Schönherr [128], Mohafezatkar Gohari et al. [129], Taktak and Özyaranlar [130], Hosseini et al. [131], and Hu et al. [132] described that because of its exceptional selectivity, recovery, and reusability after regeneration, xanthan gum is

a phenomenal biomaterial for the immobilization of heavy metals and an adsorbent of cationic dyes. Moreover, xanthan can also be used for developing edible films and coatings for the shelf-life extension of agriculture and horticulture produce [133–135]. Palaniraj and Jayaraman [119] claimed in their study that by using ultrafiltration after fermentation, the consumption of energy while recovering xanthan gum can be reduced by 80%. The main challenges involved in producing xanthan gum through microbial fermentation are viscosity obstacles. They also concluded that by employing a centrifugal-packed bed reactor, the viscosity problem can be overcome. Additionally, it was found that membrane-assisted deposition significantly increased membrane flow while using fewer accumulating solutes, leading to a significant increase in separation efficiency.

2.4. Microbial β -Glucan

Traditionally, based on raw materials, the isolation of β -glucan is grouped into cereals and non-cereals with varying compositional structures. Additionally, certain microorganisms can also create exopolysaccharides, that may be able to meet demand on an industrial scale. Exopolysaccharides from microorganisms are advantageous replacements for natural plant polysaccharides because of their distinctive metabolic characteristics. The source from which beta-glucan was acquired affects its characteristics. Industrial scale-ups of β -glucan have some constraints—notably, lengthy extraction times and high costs—associated with the process [136]. This microbial biopolymer exists both intracellularly (typically as a storage unit of carbohydrates) and extracellularly (generally as a capsule or as slime layers and biofilms). Furthermore, there are two types of microbial beta-glucans: linear and branched. Singular β (1-3) or β (1-6) glucose units may make up linear beta-glucans. Branched beta-glucans are identified by the combination of β (1-3) and β (1-6) connections [137]. Zhu et al. [136] summed up the production of β -glucan using different processes and compared the yields and production times. The biological activity of obtained β -glucan depends upon raw material, manufacturing processes, and purifying techniques [17,18,32]. β -glucan is a significant antifungal agent for crop protection. Chavanke et al. [138] reported the valuable impact of β -glucan in plant defense pathways, resistance against disease-causing microorganisms, and in response to changing environmental circumstances. Anusuya and Sathiyabama [139] observed the antifungal effect of β -glucan against the destructive fungus *P. aphanidermatum*, which mainly harms crucial crop plants. Similarly, Jayasekara et al. [62] and Anusuya and Sathiyabama [140] reported the antifungal efficacy of β -D glucan against the *Saccharomyces cerevisiae* strain and in the prevention of rhizome rot disease of turmeric, respectively. Vetvicka [141] examined the impact of β -glucan against environmental toxins like mycotoxin, aflatoxin, and depleted uranium.

2.5. Alginate

Alginate is majorly extracted from seaweed species, e.g., *Sargassum cristaefolium*, *Laminaria digitata*, and *Ascophyllum nodosum* [13,38,39], and from some bacterial strains, e.g., *Pseudomonas* spp. and *Azotobacter* spp. Alginate is an unbranched water-soluble hydrocolloid that belongs to the polysaccharide category. Guluronic and mannuronic acid-repeating monomeric units are adjoined by glycosidic connections to form alginate. The arrangement and composition of monomers designate the overall characteristics of alginate [142]. Alginates could provide a cross-link (egg-box) structure through ionic interactions and trapping cations. This chelating structural arrangement provides alginate with the capability of quenching heavy metals from wastewater. Hydrogels can be formed from alginate with the addition of calcium ions, which are usually stimulated by the incorporation of acids such as acetic acid. The potential of alginate-based hydrogels and their usage in the removal of dyes and heavy metals have been extensively studied by numerous researchers [143–150]. Furthermore, alginate is considered to remove toxic pollutants from wastewater [151,152]. Also, after contaminant elimination, algal biorefinery is a sustainable approach to recovering biochemicals (carotenoids, acetic acid, lactic acid, and eugenol), bioenergy (biohydrogen, biomethane, bioethanol, and biogas), and biomaterials

(biochar, films, coatings, and carbon fiber) from biomass [153,154] from algal biomass. As for environmental applications, Lu et al. [155] developed sodium alginate beads for wastewater treatment, which were pH-sensitive and had controllable swelling behavior, using a post-cross-linking approach. The smart polysaccharide was found to be efficient for Cu^{2+} , Ag^+ , Fe^{3+} , and methylene blue with a maximum adsorption capacity of 54.9, 82.8, 135.5, and 572.7 mg/g, respectively. In another study, Da Cunha et al. [156] fabricated pH-stimuli-responsive alginate/chitosan microcapsules containing linseed oil for the active corrosion protection of carbon steel. Benzotriazole, used as a corrosion inhibitor, was added through a layer-by-layer approach. The use of such smart biopolymers, known for their instantaneous response to pH variations, led to an observed enhancement in the release of the corrosion inhibitor at pH levels below 5. In the study conducted by Gopishetty et al. [157], sodium alginate and polyvinyl alcohol were used to create thin, porous hydrogel films with tiny pores. Due to the stimuli-responsive properties of sodium alginate, these smart hydrogel films demonstrated an ability to regulate the dimensions of the pores in response to changes in pH, thereby enhancing their efficiency in the process of separation. From advanced drug delivery systems to adaptable separation membranes, smart biopolymers hold great promise in shaping the future of technology and science. As ongoing research delves deeper into their potential, we can anticipate even more ground-breaking developments that capitalize on their unique properties. There are some limitations involved in using alginate as a biomaterial, such as mechanical stability, broad ranges of pore size distribution, mechanical stability, and osmotic swelling when subjected to physiological conditions. Additionally, due to changing environmental conditions, it is susceptible to variability in the proportion of guluronic to mannuronic acid residues and their molecular weight [63,158]. Contreras-Abara et al. [63] found that under diazotrophic conditions, its yield can be increased, and its constant molecular weight can be controlled by utilizing a continuous culture approach.

2.6. Poly (D/L- γ -Glutamic Acid) (γ -PGA)

Poly (γ -glutamic acid) is considered one of the smartest microbial biopolymers due to its distinctive structural characteristics and applications. γ -PGA is an optically active polyamide that is structurally composed of D-L glutamic acid adjoined by a peptide bond. γ -PGA Poly (γ -glutamic acid) and Poly (α -glutamic acid) are two isomeric arrangements usually extracted extracellularly through a reaction of glutamic ester monomers with an appropriate producer bacteria under optimum fermentation conditions [23,24]. The availability of free carboxyl and amine groups in γ -PGA at specific pH ranges makes it a suitable biopolymer to capture cations, especially heavy metals from noxious environments [159]. In the realm of environmental research, its emerging directive is to make sustainable material from the waste stream. γ -PGA can be used for multifarious environmental goals: in bioremediation [160,161]; as a bio-flocculant agent [65,162]; for wastewater treatment [163] or soil sedimentation [164]; as an anti-freezing agent [165] or antifungal agent [166]; for the construction of filter membranes [167,168]; and as biodegradable green plastic [169]. Although the microbial fermentation of γ -PGA has been extensively researched, costs related to manufacturing, particularly those associated with substrates and processes, continue to be high [170].

2.7. Pullulan

Pullulan is a fungal-based microbial biopolymer that belongs to the family of exopolysaccharides. It is extracted with fermentation approaches by utilizing the fungal strain *Aureobasidium pullulans*. Pullulan is comprised of replicating units of maltotriose adjoined jointly by α -(1,6) glycosidic joinings. Maltotriose is an oligosaccharide, which is further composed of three glucose units adjoined by (1,4) glycosidic joinings [171]. Elevated fermentation-broth viscosity, melanin coloring, and pullulanolysis during fermentation are the main issues encountered during the manufacturing of pullulan [172]. Other than this, the high cost of feed is a major challenge involved in producing pullulan. To overcome

this, inexpensive lignocellulosic substances can be used as carbon sources for microbial fermentation [173]. Pullulan can endure high heat loads, has a versatile range of viscosities and solubilities, and is generally regarded as safe by monitoring authorities. It embraces strong adhesive attributes and has the capacity to develop non-odorous, semi-opaque, and oxygen-proof films [125,174]. Pullulan exhibits applications in the bioremediation of industrial waste streams [29], biosorption of heavy metals [67,175,176], harmful dyes [177–179], antibiotics [180,181], and other pollutants [182] in water due to its robust adhesive attributes. The use of synthetic polymers for food packaging has increased over time due to their mechanical and thermal attributes, but the decomposition of these polymers leads to the production of harmful gases [183]. One of the major uses of pullulan is to make antimicrobial films to preserve food [184–189].

2.8. Chitosan

Chitosan belongs to the family of polysaccharides. It is one of the most researched biopolymers due to its bioactivity and is known as a non-migratory bioactive polymer (Steven and Hotchkiss 2003). The deacetylated version of chitin, poly-(14)-N-acetyl-D-glucosamine, is a natural biopolymer attained from crab shells and lobsters by engaging fungal strains (Table 2) subsequently through succeeding processes of demineralization, deproteinization, and deacetylation [190]. The solid-state fermentation process has been considered a viable approach to producing chitosan from fungal stains since it allows for substantial product concentrations and has fewer apparatus requirements than liquid-submerged fermentation. Nevertheless, solid-state fermentation has its own limitations like rapid mass transfer, and, more importantly, heat exchange issues, which become crucial on an industrial scale [191]. Another advantage of producing this microbial biopolymer from fungal sources is its uniformity, convenient handling, efficient harvesting, and availability over the entire year, as well as its improved physicochemical attributes [192]. Various research analyses studied the impact of chitosan as an antimicrobial and antifungal agent and its potential to make edible films and coating solutions for diminishing the post-harvest losses of fruits and vegetables [190,193–197]. Other potential applications of chitosan for the environment are as a plant growth regulator [198–200], a flocculating agent for dye and heavy metal reduction [201–205], a water purifier [206,207], and as a bioremediation agent [208–210]. Szymańska and Winnicka [211] reported the stability concern of chitosan as a biomaterial, referring to the degradation of chitosan during storage due to the breakdown of its functional group. The degradation of chitosan is significantly influenced by both intrinsic and extrinsic factors. It is suggested to improve the stability blending of chitosan with other hydrophilic biopolymers.

2.9. Polyhydroxyalkanoates (PHA) and Polyhydroxybutyrate (PHB)

PHA and PHB come under the type of polyesters that are intracellularly extracted by both bacterial and fungal strains. PHB is one of the forms within PHA. Among both, PHA attracts more interest from both industrialists and academia because of its wider range. PHB has limited flexibility, poor thermal stability, and a slow degradation rate as compared to PHA. Worldwide, many investigators have isolated PHA and PHB with the aid of diverse strains (Tables 1 and 3). PHA is usually comprised of linear-chained repeating (R)-3-hydroxy fatty acid units adjoined together by ester bonds. PHA is categorized into short chains (C3–C5) and medium chains (C6–C14) as per their carbon chain length. Zheng et al. [212] and Mohapatra et al. [21] extracted PHA by both submerged and solid-state fermentation. The higher yield was conveyed by solid-state fermentation. Moreover, a significant difference was noted in its thermal, structural, and morphological properties. Also, the selection of a raw material as a carbon source directly influences the quality of the microbial biopolymer. PHA functions as a storage unit and serves as a terminal electron receptor for bacteria under stress conditions [213,214]. PHA is effectively being employed for the formation of bioplastic due to its biodegradability, thermoplasticity, and bio-tolerance attributes [215,216]. Dhanania et al. [217] developed PHB nanoparticle-based scaffolds and

concluded its benefits for tissue engineering. Meanwhile, PHA could be regarded as an alternative to conventional plastics, which supports diminishing the use of synthetic polymers. Othman et al. [218] explored the potential of PHA-based degradable mulch film in rice-seed germination. Kelwick et al. [219] designed a protease biosensor based on AL-PHA beads for the detection of proteolytic activity. Amanat et al. [220] analyzed the long-term potential of diverse types of PHA-based material for bioremediation. Apart from this, PHA can also be used for purification processes [221,222]. Tanadchangsang et al. [53] observed the biodegradability of both PHA and PHB in seawater by calculating the amount of carbon dioxide collected from decomposition operations. The main drawbacks of producing this microbial biopolymer are the expensive feed and inadequate thermal and mechanical properties, mainly of PHB. Improvements to the substrate types, supplying methods, growth conditions, and/or genetic modifications can lead to much improved traits [223].

2.10. Polylactide (PLA)

Poly lactide or polylactic acid, also known as PLA, is a microbial biopolymer that functions identically to polyolefins and is capable of being processed utilizing standard approaches like blow molding and protrusion to produce green bioplastics. Polylactic acid comes under the class of polyester. It is comprised of lactic acid monomers. Sugars are generally converted into lactic acid with the aid of bacterial and algae strains and are afterward polymerized to polylactic acid [46,47]. A study by Balla et al. [224] concluded that advanced ring-open polymerization with catalysts like tin and zinc is beneficial to declining the cost of PLA. PLA is a biodegradable and biocompatible polymer that exists in two enantiomeric forms L-PLA and D-PLA can be selected for material properties. PLA is a promising biopolymer that can be extracted from municipal waste [225], lignocellulosic [226], and food waste streams with the aid of enzymatic and fermentation processes. Most waste biomass is comprised of the prevalent natural flora of lactic acid bacteria. Therefore, it can be anticipated that sugars in biowaste are naturally fermented to lactic acid [225]. Menezes et al. [227] explored the performance of PLA in protracted marine environments. Zhang et al. [228] emphasized the use of PLA-based films as an environmentally satisfying alternative to traditional plastic mulch. Another notable application of PLA-based fibrous membranes was analyzed for oil–water separation by Mo et al. [229]. In comparison to polymers made from petroleum, this microbial biopolymer is high-priced and has inferior mechanical characteristics. Now, copolymerization can be used to overcome this difficulty and to scale up at an industrial scale [230].

3. Characteristics of Microbial Biopolymers

Biopolymers produced by microorganisms offer a variety of roles for organisms. The expenditure of generating biodegradable substances as well as the expense of recycling waste can be decreased by using agricultural and industrial waste as substrates for the production of microbial biopolymers. Agricultural waste such as rice straw, maize cobs, oats, fruit peels, and molasses, and industrial waste such as wastewater from dairy processing, the textile and pharmaceutical industries, seafood, and slaughter waste, can be used to make biopolymers that are sustainable, bio-functional, biostable, and biologically compatible [231–236]. An overview of the production of microbial biopolymers from agro-industrial waste is illustrated in Figure 1.

Some of its features are as follows:

- (i) They can adapt to altering environmental circumstances and be modified accordingly [237,238].
- (ii) Microbial biopolymers such as proteins or polypeptides act as catalysts in numerous biochemical reactions. This helps to decline the activation energy when used in the chemical reaction. So, these catalysts enable microorganisms to breakdown nutrients and produce essential nutrients for cellular pathways [239].
- (iii) They are storage factories that reserve energy and permit microorganisms to acclimate extra energy in case of metabolic demand [240].

- (iv) They act as defensive associates for microbial cells and guard the cells against the environment. In other words, microbial biopolymers act as biofilms and stick to the surfaces of cells, defending them from physical and chemical stresses [241,242].
- (v) Microbial biopolymers act as intermediaries for transmission between microorganisms and their environment. They assist in receiving and sending signals to organize their behaviors and their response to alerting environments [242].

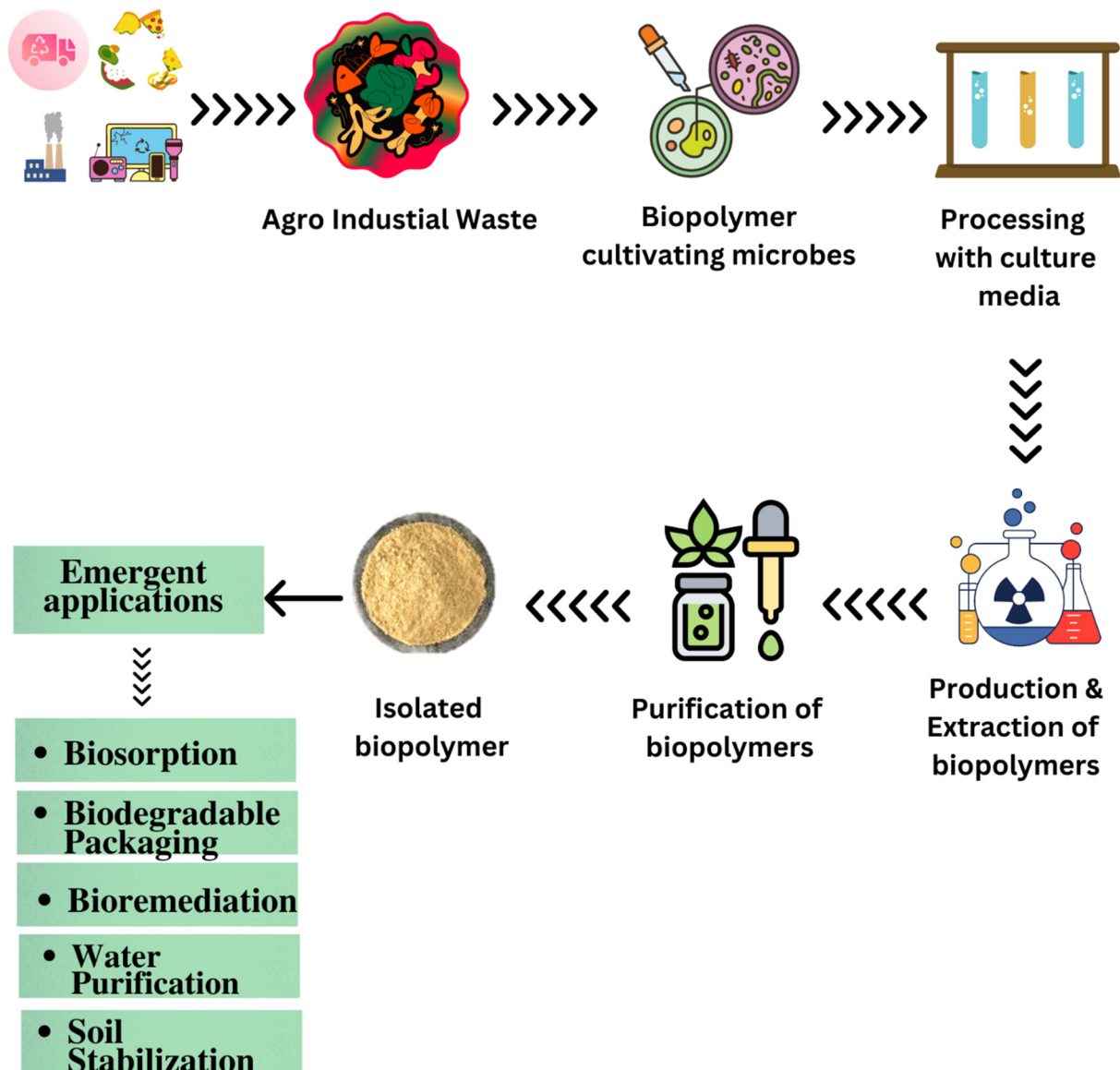


Figure 1. Overview of microbial biopolymers production from agro-industrial waste and its environmental applications.

4. Factors Influencing the Production of Microbial Biopolymers

Microbial biopolymers have garnered considerable attention lately because they have the prospect of serving as alternates for synthetic polymers. Several aspects influence the fabrication of microbial biopolymers, and they can be split into two major categories: intrinsic factors and extrinsic factors (represented in Figure 2).

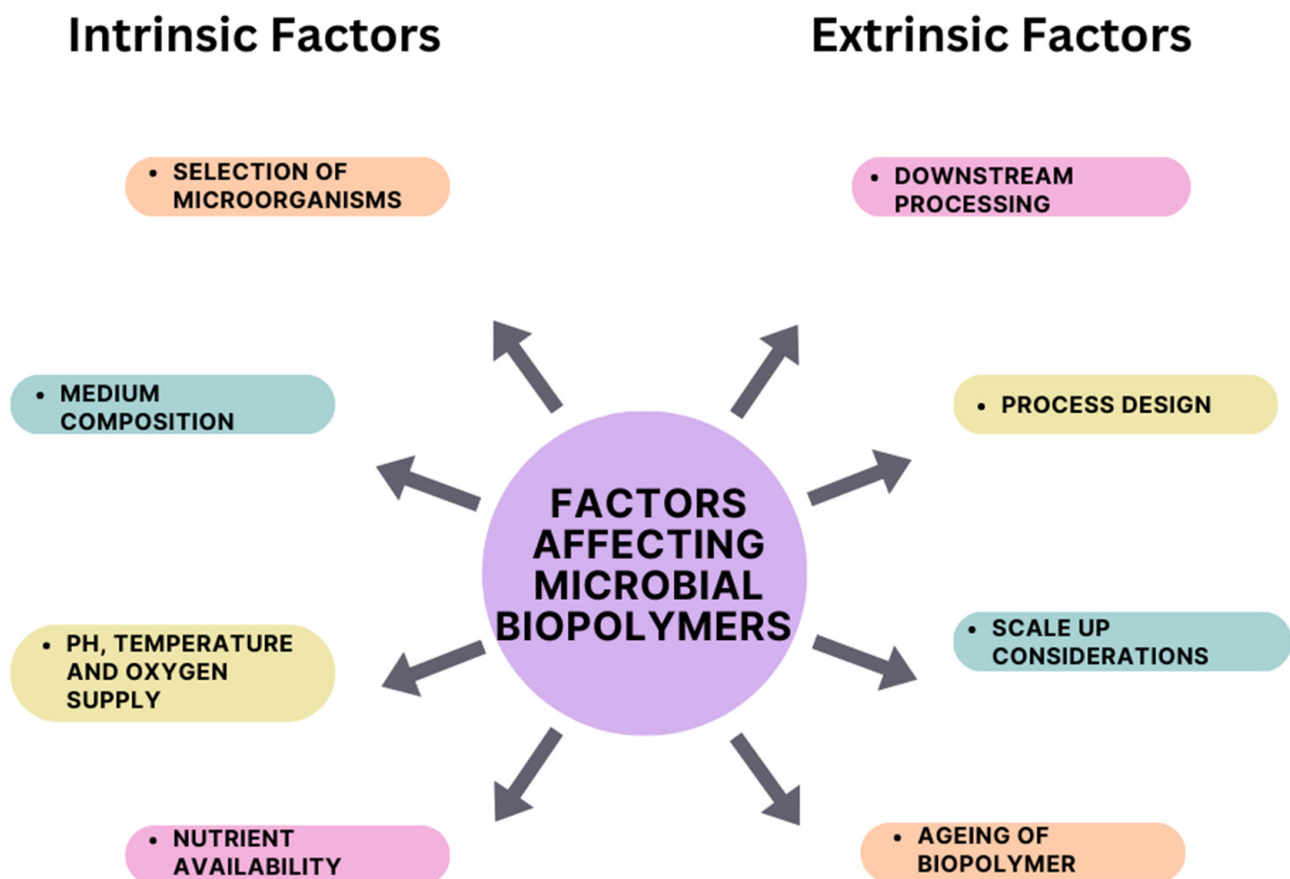


Figure 2. Factors influencing the fabrication of microbial biopolymers.

4.1. Intrinsic Factors

(i) Selection of microorganisms: The selection of microbial strains plays a vital role in the fabrication of biopolymers. There is only a limited number of commercially available strains allowed by the Food Drug Administration (FDA) for use in the fabrication process. The effectiveness, yield, and functional, mechanical, and rheological properties are directly reliant upon the selected microbial strain and its metabolic pathways [10].

(ii) Medium composition: One of the most significant factors for effective microbial fermentation is the medium composition [243]. An adequate supply of carbon and nitrogen in the culture medium is the most significant factor for the production of microbial biopolymers. Generally, microbes use polysaccharides such as glucose, sucrose, and fructose as carbon sources, as well as amino acids and ammonium salts as nitrogen sources, depending upon the type of biopolymer. Appropriate carbon-to-nitrogen ratios are desirable for the cultivation of microbial biopolymers [244]. Moreover, microbes require nutrients, minerals, and trace elements for the synthesis of microbial biopolymers (Table 4). The right concentrations of nutrients and trace elements like beef extract, yeast extract, sulfur, iron, and phosphorus are obligatory for the microbial metabolic pathway. Additionally, the medium must be free of any elements that can interfere with microbial action. Any imbalance leads to creating a disturbance in the metabolic pathway, which in turn influences the production of biopolymers [7,10,245,246].

(iii) pH, temperature, and oxygen supply: The yield and characteristics of microbial biopolymers can be reformed with the supply of oxygen. Several factors, including the microorganism, there are several pHs as well as temperature levels that are ideal for fabrication. Microbial growth rates and the fabrication of biopolymers could be impaired by deviations from the ideal circumstances.

4.2. Extrinsic Factors

(i) Downstream processing: The overall production of biopolymers is influenced by various downstream processes; filtration, precipitation, and extraction directly affect the quality of biopolymers [247]. The extraction of a biopolymer from agro-industrial waste provides less yield as compared to extraction from commercially utilized materials. Extraction of biopolymer by solvents and multiple steps in downstream processing raise the end cost of biopolymer [248]. For example, Pérez-Rivero et al. [249] and Koller [250] concluded in their studies that there are several processes in the manufacture of PHAs, and downstream processing can make up half of those steps' production costs. Periodically, the temperature step involved in downstream processing leads to a deteriorating effect on the attributes of some biopolymers.

(ii) Process design: The final attributes of fabricated biopolymers depend upon various process factors such as agitation techniques, the type of bioreactor employed, inoculum density, feeding methods, mass flow, enthalpy of stream, and processing time [251]. Simple batch reactors, continuous or fed-batch systems, and semi-continuous are possible types of bioreactors employed for the production of microbial biopolymers. In terms of the layout, scalability, ease of inspection, control, and the particular needs of the biopolymer being produced must be considered [9,252].

(iii) Scale-up considerations: There are complications in repositioning lab-scale biopolymer production on an industrial scale. For prosperous large-scale production, components like conserving constant requirements, precluding contamination, and improving nutrient and oxygen transportation are paramount [7].

(iv) Ageing of biopolymers: After the fabrication of the biopolymer, it experiences changes in its structural and rheological properties over time. This process is known as the aging of biopolymers. Changes in crystallinity and physicochemical attributes are directed towards the weakening of biopolymers. Nagaraja et al. [253], Deroine et al. [254], Siviello et al. [255], Leceta et al. [256], Santos et al. [182] and Cui et al. [257] observed the impact of aging on poly(3-hydroxybutyrate-co-3-hydroxyvalerate), alginate, chitosan, bacterial cellulose and polylactic acid, respectively.

5. Role of Microbial Biopolymers in Wastewater Treatment Processes

Wastewater describes any water that has been contaminated by industrial processes or human activities, including both residential and commercial sources and natural sources, such as stormwater runoff and infiltration or inflow into sewer systems [258]. Wastewater contains a range of contaminants, including inorganic pollutants (heavy metals and rare earth minerals), organic pollutants (dyes, food, detergents, pesticides, herbicides, and pharmaceuticals), and other pollutants (oil, radioactive waste, spill, grease, etc.), which have detrimental effects on the environment and human health [259]. Until now, step-by-step processes like preliminary, primary, and secondary treatment have been employed to ensure water meets the required quality standards for safe discharge or reuse [258]. Various approaches have been tested in the removal of contaminants, including aerobic and anaerobic biological methods and the use of physical and chemical treatments. Coagulation and flocculation comprise fundamental stages in the removal of large, coarse, solid materials, like suspended solids, heavy metal ions, and dye molecules. Oxidation methods tackle the removal of organic impurities, while adsorption mechanisms have proceeded to capture soluble particles. Membrane-based treatment technologies have also demonstrated the capacity to separate impurities from wastewater, enhancing overall water quality [260]. Recently, the use of microbial biopolymers has gained significant attention as a value-added and sustainable approach to wastewater treatment. By acting as filtration media, adsorbents, coagulants, and flocculants, microbial biopolymers can be integrated into various stages of the treatment process, potentially further enhancing the efficiency and effectiveness of wastewater treatment methods [171]. The upcoming subsections will delve into the diverse roles of microbial biopolymers in wastewater treatment.

6. Applications of Microbial Biopolymers

6.1. Microbial Biopolymers as Adsorbents

Adsorption is a surface phenomenon that has gained popularity in water treatment in recent years. It is a well-known equilibrium separation process recognized by its simplicity, effectiveness, and efficiency [261]. This process is favored because it does not require the use of extra chemicals, excess water, or energy, thereby allowing for a low operating cost [262]. Synthetic polymers are generally derived from coal and petroleum, which are unable to fit in recycling systems. Contrarily, microbial biopolymers outperform petroleum-based polymers in terms of affordability, environmental sustainability, and usability [263]. Microbial biopolymers are composed of a variety of functional groups, including methoxyl carboxyl, phenolic hydroxyl, amines, and hydroxide. Due to chelating metal ions establishing surface complexes, these functional groups of microbial biopolymer-based adsorbents enhance the adsorption efficacy of pollutants from different samples [264]. Generally, adsorption occurs due to attractive forces between the adsorbate, which is the compound being adsorbed, and the surface of the adsorbent, the compound to which the adsorbate gets attached. Up to date, a variety of adsorbents have been used, and the common types can be classified depending on the material nature. Thus, adsorbents can be from organic, mineral, or natural origins [261]. Among the natural group, microbial biopolymers and biopolymer composites, (Table 5) play a significant part due to their porous structure, highly specific surface area, durability, and cost-effectiveness. Additionally, their abundant functional groups present on the surface can speed up decontamination and the removal of soluble particles, greasy substances, dyes, and other pollutants in water. Likewise, these functional groups have an affinity to combine with heavy metals like mercury, copper, cadmium, lead, nickel, chromium, and zinc. Biopolymers also offer a promising solution to address emerging contaminants, particularly surfactants, in wastewater. Biswas and Pal [265] discussed the use of biopolymers such as chitosan, alginate, tannin composites, and more for the removal of surfactants. Recent progress in the development of chitosan-based adsorbents, shedding light on their remarkable potential for various pollutant removal, such as heavy metal ions, and cationic and anionic dyes, has been emphasized by da Silva Alves et al. [266]. As highlighted by Benavente et al. [267], the abundant amino and hydroxyl groups on the surface of chitosan can be used to chelate heavy metal ions, specifically Cu^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+} , with a maximum adsorption capacity of 79.94 mg/g, 109.55 mg/g, 58.71 mg/g and 47.15 mg/g, respectively. Additionally, alginate, with its hydroxyl and carboxyl groups distributed across its surface, can capture metallic ions through an ion-exchange mechanism [268]. However, despite such unique advantages, limited functionality, including poor mechanical, chemical, and physical properties, has been observed. Therefore, biopolymers are often subject to modification using various synthetic or natural monomers, and they are combined with diverse materials for applications in water treatment [259]. As a low-cost adsorbent, cellulose can be chemically modified by esterification, etherification, oxidation, halogenation, and chelation. In the context of chelation, amine, carboxyl, amide, and imidazole binding ligands were seen to have better efficiency, owing to their large surface area, cost efficiency, and sustainability [171]. Another promising way to further enhance biopolymer adsorbents' ability to remove heavy metals and dyes is the utilization of low-cost sorbent hydrogels. A sodium alginate/polyethylene amine compound hydrogel has shown an adsorption capacity of 322.6 mg/g and 344.8 mg/g for the absorption of Cu^{2+} and Pb^{2+} ions, respectively, in wastewater [269]. In another case, a sodium alginate/polyethyleneimine hydrogel was used for dye adsorption and demonstrated the excellent removal performance of methylene blue with a maximum absorption capacity of 400.0 mg/g. Within 30 min, approximately 99% of the dye was removed [270]. Furthermore, graphene oxide (GO) was encapsulated in a sodium alginate/polyvinyl alcohol compound. Used as an effective adsorbent for removing Cu^{2+} and UO_2^{2+} , the hydrogels showed a maximum absorption of 247.16 mg/g and 403.78 mg/g, respectively [271]. In another research, GO was used to formulate three-dimensional graphene oxide porous biopolymer gels, which foster the establishment of hydrogen bonding and hydrophobic interactions.

This 3D network structure provides abundant active sites for the effective adsorption of cationic dyes and heavy metal ions. Another interesting technique was highlighted by Wang et al. [272], which involved the use of aquatic sodium alginate for the gelation of heavy metal ions. In this study, alginate showed the fast gelation of Pb^{2+} , Cu^{2+} , and Cd^{2+} within less than 10 min. The resulting gel–liquid separation from wastewater was achieved smoothly through gravity. Magnetic adsorbents are becoming increasingly favored in water treatment. Their rising popularity can be attributed to their capacity to enhance adsorption efficiency, minimize adsorbent wastage, and simplify separation through the use of an external magnetic field [273,274]. Abdul Rahman et al. [275] developed magnetic cellulose, chitosan, alginate, and composite hydrogel beads. The bio-sorbent demonstrated strong potential for treating heavy metal-contaminated wastewater comprised of Ca and Fe ions and showcased enhanced thermal stability when compared to raw cellulose and chitosan. The mechanical resistance of some naturally derived microbial biopolymer-based membranes is poor. This can be overcome by embedding it with compatible nano biomaterials [276]. For instance, chitosan is an interesting biopolymer for this purpose due to its film-forming ability, biocompatibility, and favorable hydrophilicity [277]. Salehi et al. [277] investigated chitosan-based membranes for adsorptive studies. They suggested the concept of cross-linking chitosan with TiO_2 to create a self-regenerating dye adsorbent. Also, cross-linking with glutaraldehyde, glyoxal, and formaldehyde was suggested to improve its solubility and mechanical attributes.

Table 5. Studies related to the use of biopolymers as adsorbents to treat wastewater.

Polymer	Pollutant	Adsorption Capacity (mg·g ⁻¹)	References
Inorganic contaminants			
Carboxylated cellulose nanocrystal/sodium alginate hydrogel	Pb ²⁺	335.3	[278]
Cellulose/PVA/Graphene Composite aerogel	Cu ²⁺	80.12	[279]
	Cd ²⁺	102.23	
	Cr ³⁺	123.02	
	Co ²⁺	62.38	
	Zn ²⁺	69.55	
	Pb ²⁺	57.16	
Thioglycolic Acid-Esterified Cellulose Nanocrystals	Cu ²⁺	4.244	[280]
Chitosan-glucose hydrogel	Co ²⁺	202	[281]
Chitosan/orange peel hydrogel	Cu ²⁺	116.6	[282]
	Cr ⁶⁺	107.5	
Xanthate-modified chitosan/poly (N-isopropylacrylamide)	Cu ²⁺	115.1	[283]
	Pb ²⁺	172.0	
	Ni ²⁺	66.9	
Cellulose/guar gum/biochar	Cu ²⁺	805.45	[284]
	Co ²⁺	772.52	
Cellulose/bentonite grafted polyacrylic acid hydrogel	Cd ²⁺	242.53	[285]
Alginate/polyethyleneimine	Cu ²⁺	322.6	[269]
	Pb ²⁺	344.8	
3D network nanostructured sodium alginate	Cd ²⁺	9.54	[286]
	Cu ²⁺	13.38	
Hyaluronic acid-supported magnetic microspheres	Cu ²⁺	12.2	[287]
	Pb ²⁺	530.54	
Xanthan gum/n-acetyl cysteine modified mica bionanocomposite	Cu ²⁺	177.2	[288]
	Ni ²⁺	51.48	
	Cd ²⁺	312.15	
Poly (Acrylamide-co-Acrylic Acid)/Xanthan Gum hydrogel	Ni ²⁺	185.0	[289]
	Cu ²⁺	100.9	
Pullulan/polydopamine hydrogels	Cu ²⁺	100.9	[290]
Sodium alginate/coffee waste	Pb ²⁺	984.4	[291]
Whey protein concentrate/pullulan hydrogel	Cu ²⁺	81.6	[292]
Polylactic acid hydrogel	Pb ²⁺	416.07	[293]
	Ni ²⁺	243.10	
Organic contaminants			
Sodium hydroxide activated acrolein/chitosan	Acid blue 93	2500	[294]
Carboxymethyl cellulose/chitosan/triethylenetetramine	Direct blue	534.25	[295]
	Congo red	519.53	
Cellulose/guar gum/biochar	Methylene blue	598.28	[284]

Table 5. Cont.

Polymer	Pollutant	Adsorption Capacity (mg·g ⁻¹)	References
Cellulose/Poly(acrylic acid)	Methylene blue	1492.99	[296]
Chitosan/polyacrylate/graphene oxide	Methylene blue	296.5	[297]
	FY3	280.3	
Chitosan/cellulose	Congo red	380	[298]
Chitosan/poly(n-vinyl-2-pyrrolidone)	Orange G	63.7	[299]
Xanthan gum/amantadine composites	Methylene blue	565	[300]
Polyaniline/Xanthan Gum Nanocomposite	Methylene Blue	22.52	[301]
Xanthan gum/polyacrylic acid/graphene oxide	Methyl violet	1052.63	
	Methylene Blue	793.65	[302]
Pullulan-graft-poly(3-acrylamidopropyl trimethylammonium chloride) microspheres	Azocarmine B	113.63	[303]
Sodium alginate-polyaniline nanotube	Methyl orange	370.4	[304]
Sodium alginate/coffee waste	Acridine orange	805.3	[291]
Crosslinked chitosan films	SDBS	714	[305]
Nanofibrillated cellulose	Cationic surfactants	462.28	[306]
Hydrogel chitosan beads	SDS	1300	[307]

6.2. Microbial Biopolymers as Coagulants and Flocculants

Coagulation and flocculation are two interrelated methods commonly known as the most economical processes used in water treatment for solid-particle removal. Despite their interconnection, coagulation and flocculation are entirely different phenomena. Coagulation is an electrostatic phenomenon that occurs through the charge neutralization of suspended particles and colloids. It is induced by adding coagulants that destabilize the particles, leading to their collision and aggregation. This, in turn, initiates the formation of flocs, which precipitate from the suspension due to the influence of gravity. Flocculation takes place to further enhance the downstream processes by creating larger and heavier flocs, thereby enhancing the effective removal of impurities. While coagulation occurs in a short time frame of less than 10 s, flocculation is a long physical process lasting about 20–45 min [274,308]. A large variety of coagulants and flocculants have been used for wastewater treatment. Commonly used inorganic coagulants, such as aluminum sulfate, aluminum chloride ferrous sulfate, etc. [309–311], have caused environmental and ecological concerns due to their generation of additional sludge volume [312,313]. Hence, microbial biopolymers emerged as a viable solution [312,314]. Among the variety classes of biopolymers, polysaccharides have garnered significant attention from the scientific community, mainly due to their functional groups present on the surface, contributing to the effective adsorption of different contaminants in the flocculation process [315–317]. As described in the recent literature, chitosan, cellulose, alginate, pullulan, xanthan gum, and their derivatives are bio-based flocculants. Those polysaccharides have shown their ability as relevant agents in the elimination of turbidity, total dissolved solids (TDS), chemical oxygen demand (COD), metal cations, inorganic anions, dyes, pesticides, minerals, microorganisms, and numerous other pollutants found in various types of wastewaters [318]. Other bioflocculants based on dextran [319–321], pectin [322,323], and lignin [324], as well as their grafted derivatives, have also been reported for color-reducing, turbidity, COD, or heavy metal ions. Table 6 provides an overview of recently reported biopolymers and their derivatives as coagulants and flocculants investigated for water treatment. With the emergence of nanocomposite-based biopolymers, reports regarding the utilization of biopolymers in their unmodified form are notably limited. This can be attributed to the very developed surface area of nanoparticles, characterized by a notable abundance of active sites and functional groups, which positively enhance water treatment [325,326]. However, despite the multiple gains in using nanoflocculants, real concerns remain about the potential environmental impacts regarding the introduction of these particles into the ecosystem. Uncertainty surrounding whether nanoparticles will induce toxic effects within the natural environment persists [318]. Recent reports highlight that direct flocculation, operating independently from coagulation, is emerging as a notably cost-effective alterna-

tive, particularly attributed to its reduced cost and environmental impact, along with its enhanced safety for human well-being and efficiency in terms of time. It is a simplified method based on the dual functionality of cationic or anionic polymers, first neutralizing particle charges and then bridging their aggregation. Unlike coagulation, direct flocculation has demonstrated its effectiveness for high levels of organic contaminants across a large pH spectrum [315,327]. Several factors and mechanisms are involved, ranging from the chemical structure, properties, and charge of both the particles to be removed and the flocculant to their concentration, the pH of the environment, temperature, mixing rate, ionic strength, and even the mechanism of the process, which can significantly influence the flocculation. Thus, despite the significant progress that has been made in understanding this process, ongoing research continues to further uncover its complexities [328].

Table 6. Studies related to the use of biopolymers as coagulants flocculants to treat wastewater.

Polymer	Pollutant	Removal Rates (%)	References
Inorganic contaminants			
Chitosan/Poly(acrylamide-acryloyloxyethyl) trimethylammonium chloride	Zn ²⁺	99.3	[329]
Sodium alginate/triethylenetetramine nanoflocculant	Pb ²⁺	97	[330]
Chitosan/acrylamide/itaconic acid/3-acrylamide propyl trimethylammonium chloride	Ni ²⁺	86.3	[331]
Cationic Pullulan Derivatives	FeO	95	[332]
	TiO ₂	75	
Organic contaminants			
Chitosan/poly (acrylamide-itaconic acid)	Crystal violet	81.6	[333]
Polyaluminium chloride/xanthan gum	Congo red	93.81	[334]
Cationic pullulan derivatives	Novadim	90	[335]
	Bordeaux mixture	98	
	Karate Zeon	80	
Cationic cellulose/bentonite	Methylene Blue	99	[336]
	Duasyn Direct Red	95	
	Acid Black 2	100	
	Crystal Violet	100	
	Basic Green 1	99	
	Crystal violet	92.2	
Carboxymethyl cellulose/itaconic acid/sodium alginate	Crystal violet	92.2	[337]
Cellulose nanocrystals	Reactive blue 19	80	[338]
Sodium alginate/methacryloxyethyltrimethyl ammonium chloride	Dissolved Organic Carbon (DOC)	35.42	[339]
Other contaminants (Water Quality Parameters)			
Sodium alginate/methacryloxyethyltrimethyl ammonium chloride	UV ₂₅₄	32.42	[339]
Xanthan Gum/Polyacrylamide /SiO ₂	Turbidity	93.95	[340]
	Total Solids (TS)	76.97	
	Total Dissolved Solids (TDS)	48.21	
	Total Suspended (TSS)	93.75	
xanthan gum/polyacrylamide	Turbidity	52.63	[341]
Pullulan/p(N-isopropylacrylamide)	Turbidity	88	[332,342]
Poly-γ-glutamic acid	Turbidity	86.6	[343]
Chitosan/Poly(acrylamide-acryloyloxyethyl) trimethylammonium chloride	Total Phosphorus (TP)	98.8	[329]
Chitosan/poly-glutamic acid	COD	44.8	[344]
	Total Nitrogen (TN)	53.4	
	TP	28.1	
	Turbidity	98.3	
Bentonite/chitosan/poly-glutamic acid	COD	86.2	[285]
	TN	80.3	
	TP	52.3	
	Turbidity	98.2	
Sodium alginate/methacryloxyethyltrimethyl ammonium chloride	Turbidity	95.96	[339]
Sodium alginate/polysilicate aluminum calcium	Turbidity	97.2	[345]
Chitosan/Poly(acrylamide-acryloyloxyethyl) trimethylammonium chloride	COD	72.5	[329]
Cellulose Nanocrystals	Turbidity	99.7	[346]
Dicarboxyl cellulose	Turbidity	80	[347]
	COD	60	
Dicarboxyl cellulose	Turbidity	99.5	[348]

6.3. Microbial Biopolymers as Filters in Membrane Processes

The capacity of microbial biopolymers to develop biofilms, set up selective barriers, and improve filtration effectiveness is the idea underlying their application as filters in membrane processes. Impaction, electrostatic contact, diffusion, and interception are prominent processes involved in biopolymer filtering [241,349]. Filtration is a method used for the separation of solid particles and large molecules from liquid suspensions through a porous barrier such as a membrane. Membranes possess selective permeability, controlling the passage of mass through their porous surfaces through interactions with the materials to be separated. The efficiency of this technique is directly linked to the size of the membrane's pores and the characteristics of the material used [350]. A wide variety of membranes with different conformations and structures are available. Membrane filtration techniques such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are distinguished by their varying pore sizes, ranging from 5000 nm in MF to 0.2 nm in RO [351]. As with all membrane filtration processes, the main downside that limits their large-scale applications is membrane fouling, which occurs due to contaminants that adhere to the membrane's surface or get trapped within its pores over time, forming a layer that hinders the flow of desired components through the membrane. This phenomenon reduces filtration efficiency as well as the membranes' lifespan and increases energy consumption [352,353]. Recently, biopolymer nanocomposite membranes have gained popularity as a promising solution for mitigating membrane fouling. They have shown improved antifouling properties by minimizing the adhesion of floculants and improving water permeability, thereby enhancing filtration process efficiency [354,355]. This, in turn, has played a pivotal role in fueling the fast growth of membrane filtration technologies and has boosted the number of publications focused on the utilization of membranes for separating oil–water emulsions [356]. The use of natural fillers such as nitrocellulose or chitosan nanoparticles within biopolymer membranes has significantly enhanced membrane stability and reduced the dosage of chemicals and the volume of sludge. Therefore, biopolymers stand out as an environmentally friendly, efficient, and sustainable alternative to conventional membrane filtration techniques [350,357]. Among the different biopolymers, hydrophilic biopolymers, such as bacterial cellulose, chitosan, alginate, and hyaluronic acid, are preferred for membrane processes due to their durability and ability to withstand corrosive substances that may be present in the wastewater. As highlighted by Galdino et al. [87], a bacterial-cellulose matrix can be used to separate almost all oil during the filtration of oily effluents and can be washed and reused up to 20 times without losing its filtration efficiency. Surface modification can further enhance retaining specific contaminants like heavy metals and dyes, thus improving the membrane's permeability and selectivity [358]. For example, Yu et al. [359] demonstrated that a modified chitosan-cellulose acetate-TiO₂-based membrane can be used for the demulsification of oil–water emulsion, reaching up to 99% in separation efficiency. As highlighted by Divya and Oh [360], recent advancements in microbial polymer thin-film nanocomposite membranes, incorporating nanofillers like carbon-based materials, metals, and metal oxides, have garnered considerable attention in the field of water purification due to their notable characteristics, including hydrophilicity, thermal stability, selectivity, permeability, and thermal resistance. However, despite advances in the biopolymeric-membrane approach, some major limitations were also observed: the potential degradation of biopolymer during extended storage periods, their requisite compatibility with the effluent being treated, and the potential high operational costs when aiming for a higher rate of solid- and liquid-phase separation [356]. Additional drawbacks, such as the potential risk of obstructing the water flow pathway due to the addition of nanomaterials; the formation of defects and non-selective porosity resulting from inadequate interaction between the polymer and nanoparticles; and the poor dispersion of fillers within the polymer matrix, leading to the aggregation and agglomeration of nanoparticle on the membrane surface or within the membrane itself, all emphasize the need for further research to address these existing challenges [355]. Table 7 summarizes recent research on membrane filtering

employing biopolymer materials. Bacterial cellulose is one of the most interesting microbial biopolymers for this application due to its large surface area, nano-porous structure, and biodegradability [15]. Faria et al. [15] investigated the exceptional quality of bacterial cellulose for eliminating microplastics by 99%, which upheld performance for continuous cycles. Qalyoubi et al. [276] addressed the most common challenges associated with novel adsorptive membranes including fouling, costs associated with the process, adsorbent regrowth, adsorption capacity, barrier permeability, rates of rejection, and specificity. They also concluded that, since many novel materials have only been evaluated in research settings up to this point, creating innovative materials for hybrid matrix membranes is still an obstacle to overcome. Exploring cheaper alternatives for adsorptive membranes could be a useful area of interest because many innovative materials are unable to enter the industry due to their high price tags. Concerning superior performance and high adsorptive capacity, agro-industrial waste is a suitable candidate to be explored for this purpose.

Table 7. Studies related to the use of biopolymers as membrane filters to treat wastewater.

Polymer	Pollutant	Removal Rates (%)	References
Inorganic contaminants			
Polylactic acid/amino-activated carbon/modified mangrove particles pH-responsive adsorptive membrane	Cu ²⁺	99.95	[361]
	Pb ²⁺	100	
	Ni ²⁺	99.95	
Cellulose acetate/chitosan/TiO ₂	Cu ²⁺	97.0	[359]
PLA/PHB/Polybutylene succinate/polypropylene carbonate/silica nanoparticles	Mn ²⁺	14.17	[362]
Cellulose acetate/nanochitosan/PEG	Cr ⁶⁺	95	[363]
Hyaluronic acid/polyamide	Na ₂ SO ₄	94.90	[364]
Organic contaminants			
Cellulose acetate/PLA/polyurethane	Methylene Blue	45	[365]
	Congo Red	60	
Cellulose microfiber/PLA/poly(butylene adipate-co-terephthalate)/maleic anhydride	Methylene Blue	97.2	[366]
Fe ₃ O ₄ /Xanthan gum/polyvinylidene fluoride	Reactive Black 5	84.8	[367]
	Reactive Red 120	73.8	
Xanthan Gum/polyvinylidene fluoride/dimethyl sulfoxide	Congo red	91.25	[368]
Cellulose microfiber/PLA/poly(butylene adipate-co-terephthalate)	Methylene Blue	58.7	[366,369]
	MB	100	
	Direct Red (DR80)	98.80	[369]
	Congo Red (CR)	100	
	Crystal Violet (CV)	100	
Sodium alginate hydrogel/graphene oxide		99.7	[370]
	Direct Orange S, Procion Red	97.8	
	mx-5B Stilbene Yellow	62.8	
	Methylene Blue	27.5	
Hyaluronic acid/polyamide	Perfluorohexane sulfonic acid (PFHxS)	93.40	[364]
Other contaminants			
Sodium alginate/tannic acid/β-FeOOH	Oil	99.64	[371]
Chitosan/bacterial cellulose/carboxyl multi-walled carbon nanotubes	Oil	97.67	[370]
	Oil	93.9	
Pristine PLA	Oil	99.6	[372]
PLA/polyethylene oxide	Oil	99.4	[373]
Cellulose acetate/chitosan/TiO ₂	Oil	97.0	[359]
	Oil	90.1	
PLA/multi-walled carbon nanotubes/graphene oxide	Ammonium-nitrogen	71.3	[374]
	Phosphate	98.6	
PLA/PHB/Polybutylene succinate/polypropylene carbonate/silica nanoparticles	Oil	22.56	[362]
	Total Dissolved Solids (TDS)	11.33	
	Turbidity	89.15	
Cellulose acetate	Sulfamethoxazole	82	[375]
	Primidone	85	
	Carbamazepine	85	
	Phenacetine	10	
	17β-Estradiol	29	

6.4. Bioremediation and Soil Stabilization

Bioremediation is an economical and time-consuming approach usually employed for degrading, neutralizing, and detoxifying contaminants predominantly from soil, water, and sediments. Bioremediation is chiefly performed by diverse means such as biodegradation, phytoremediation, bioaugmentation, and biostimulation. These incorporated methodologies usually accelerate metabolic activities and remediate contaminated sites [376,377]. Biosorption can be accompanied by a variety of other techniques, which boost the recovery or removal of pollutants such as metalloids [378]. For example, there are challenges involved in removing metalloids. However, these challenges can be overcome by the formation of metalloid complexes with microbial biopolymers. Due to electrostatic interaction, the generation of stable complexes between metalloid and microbial biopolymers takes place [379]. Many microbial biopolymers contain negatively charged functional groups that help to bind metals, such as hydroxyl groups (OH^-) on the matrix of bacterial cellulose, carboxyl groups (COOH^-) in hyaluronic acid, xanthan gum, and alginate. Also, the charges present on some microbial biopolymers vary as per the pH of the surrounding environment. For example, at an acidic pH, chitosan gains hydrogen (H^+) and becomes a positively charged ammonium group (NH_3^+), and at an alkaline pH, chitosan loses hydrogen ions and becomes an uncharged amine form (NH_2) [380]. Depending upon the charge, microbial biopolymers can be employed for multiple applications, which are cited in previous sections. Additionally, microbial biopolymers act as nutrients, which directly promotes the microbial activity of microorganisms involved in the bioremediation process and allows them to thrive and flourish in a variety of unfavorable conditions. Furthermore, some microbial biopolymers such as PHA and PHB produce metabolizing enzymes under particular nutritional and environmental stresses, which helps to upsurge bacterial survival during the bioremediation process [11].

Soil stabilization is an approach for altering the physiochemical attributes of the soil; it enhances the soil's effectiveness in terms of physical aspects. Biofilm-oriented bioremediation is a potent tool for the removal of environmental pollutants. Soil stabilization promises the improved structural stability of soil [381,382]. Microbial biofilms are collections of grouped microbial cells wrapped in an extracellular polymeric substance (EPS) matrix that they have self-assembled. Because they are resistant to harsh environments, biofilms serve as a shield for safeguarding microbes from factors such as exposure to ultraviolet rays, excessive temperature, elevated salinity, and abnormal pH [242]. Numerous kinds of unwanted substances have polluted both the ecosystems of land and water. The majority of these pollutants are polymers of polycyclic aromatic hydrocarbons and total petroleum hydrocarbons, which are generally considered a threat to public health [383,384]. Industrial waste such as dyes and wastewater streams are usually comprised of the aforementioned pollutants and are responsible for polluting the soil and water. The primary approaches to eliminating the metals from polluted soil are thermal desorption, adsorption, precipitation by chemicals, ion exchange, and electroplating accumulation [385]. With the advent of recent developments in microbial biopolymers, the latest developments in the industry are investigating the strategic application of microbial biopolymers and bioremediation methods as environmentally satisfactory alternatives for soil stabilization. Microbial biopolymers have prospective benefits in terms of sustainable development, biological degradation, and minimal carbon footprint [386]. Due to their distinctive qualities and compatibility with the environment, various biopolymers have been employed for dust control, erosion control, and strengthening soil [387]. For instance, xanthan gum has been used for strengthening and stabilizing soil [388–392]. Also, chitosan has been employed to minimize permeability, eliminate heavy metals, stabilize soil, hasten the separation of organic matter, and limit soil erosion [393–398]. Microbial biopolymers could transform soil engineering approaches, providing more environmentally friendly choices for persistent soil stabilization as well as encouraging a more sustainable future.

7. Challenges and Future Perspectives of Microbial Biopolymers in Environmental Applications

Microbial polymers are an attractive substitute for chemically derived materials. However, scaling up their production from a laboratory to an industrial scale is very challenging. Several variables—notably the cost of substrates, the amount of biopolymer produced over feed rate, and the expenditures of downstream processing, among others—determine how successfully biopolymers may be scaled up and if they are economically feasible to produce at an industrial scale [14]. The major challenges in the process are the production cost and the extraction of a pure biopolymer from a complex mixture. Acquiring microorganisms that can use inexpensive as well as easily accessible raw ingredients is a crucial phase in making microbial biopolymer manufacturing economically viable [399]. Using waste raw material for biopolymer production is very attractive and can largely address the issue of the high cost of raw ingredients. Moreover, the use of genetically modified strains and omics techniques to enhance the fermentation yield could greatly help to minimize the overall production cost [400].

The dewatering process of biomass following its cultivation represents one of the foremost operational expenditures in polymer recovery. Undoubtedly, one of the most popular approaches for this is settling. Gravitational settling is the most straightforward and inexpensive method, but due to the small molecule size of microbial biopolymers, filtering by membranes could potentially be employed, accompanied by centrifugation. However, it should be accurately optimized to limit the enhancement of operation costs [401].

In general, optimizing bioprocess at a pilot scale, coupled with techno-economic analysis, could help in resolving many industrial challenges.

In silico methods should be also employed to simulate the production and secretion of bacterial polymers based on the huge availability of data. This could offer valuable insights into the regulatory framework required for their safe application—a framework that is absent at present [400].

Moreover, legislative and policy unpredictability could make it challenging to meet environmental goals. Uncertainty alters the political economics of environmental policy. The acceptability, development, and scalability of microbial biopolymers also depend upon the system. The system is comprised network of actors (business organizations, research groups, policymakers, and regulatory bodies). In a nutshell, the setting up of new supply chain-hosting actors requires a lengthy approach to the development and implementation of novel economic models, among other aspects [402]. Last but not least, environmental applications come with the challenges of handling data that require computation and vast information storage units. Rodila et al. [403] commented on the features of big data, referring to the 5V principle (Volume of data, Velocity of data accumulation, Variety of data by different sources, Validity and precision of data, Value and Purpose of data). Numerous environmental applications will be more efficiently utilized by the correct mathematical framework and its mapping across different computational systems [403]. A deep understanding of the interaction between diverse ecosystem complexities and environmental and biodiversity uncertainties is required, which makes it challenging to design a model to anticipate and adapt to changes in the future to produce desirable outcomes [404,405].

8. Conclusions

In contrast to the information available on physical and chemical methods, the amount of information available on the environmental implications of microbial biopolymers is very limited. As a result, information on significant biopolymer production, recovery, processes, and the potential of environment applications was insufficient. This updated review offers exclusive knowledge of the growing interest in environmental applications of microbial biopolymers. Using biopolymers is an opportunity to solve environmental issues and an effective approach to the circular bioeconomy. There is still a large gap between industry and academia. Many research studies were conducted on a laboratory scale only.

A vast approach is required to commercialize the technology on a mass scale. Moreover, government organizations and regulatory agencies need to establish procedures for the maturation and placement of microbial biopolymers to benefit from application in practice and monetary profits.

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