Biopolymer in Wastewater Treatment

Jasdeep Singh, Shubham Kumar, and Swati Sharma

Abstract Water is the most essential resource on the planet, as it is required for the survival of all living organisms. Apart from the need for water for drinking, it is an essential component of modern societies with agricultural and industrial sectors heavily dependent on it. However, the inappropriate release of a range of harmful organic and inorganic contaminants from untreated industrial, agricultural, and domestic wastewater has a negative impact on water resources and thus poses a great risk to aquatic systems, animal, and human health. Organic toxics like dyes, as well as heavy metals including cadmium, chromium, cobalt, copper, lead, mercury, nickel, tin, and zinc, may be present in our water supplies, posing major health risks to all living species. Some methods, including adsorption, coagulation, flocculation, ion exchange, and membrane filtration, precipitation and co-precipitation, and solvent extraction, have been tested for the removal of these toxic pollutants. However, the capital cost for these treatment methods is very high and require synthetic toxic reagents. Biopolymers have been recently suggested for wastewater treatment because of their renewable properties, sustainability, biodegradability, and non-toxicity. Biopolymers can also be combined with a variety of reinforcing elements (antioxidants, natural fibres, pigments, and micro-, nanoparticles of inorganic fillers) to create unique composites with enhanced characteristics. In this chapter, we describe the application of various natural biopolymers and grafted copolymers to remove heavy metals, dyes, oils, other chemical or drugs, and turbidity from the wastewater, as well as challenges and future perspectives in the development of novel biopolymers.

Keywords Biopolymers · Wastewater treatment · Bio-flocculants · Polysaccharide polymers · Grafted flocculants

---

J. Singh · S. Kumar · S. Sharma (✉)
University Institute of Biotechnology, Chandigarh University, Mohali 140413, Punjab, India

A. K. Nadda et al. (eds.), *Biopolymers*, Springer Series on Polymer and Composite Materials, https://doi.org/10.1007/978-3-030-98392-5_15

1 Introduction

Annually, almost 140 million tonnes of synthetic polymers, such as plastics, are produced around the world, and contribute to water pollution. Because they are incredibly stable, their degradation being nearly unattainable, the synthetic polymer has been recognised as a major setback for wastewater treatment [14].

Further, the water resources are also polluted with different heavy metals, for example, cadmium, chromium, cobalt, copper, mercury, nickel, lead, and zinc and dyes, [45] which are found in industrial and agricultural effluents and pose substantial health risks to living beings [33].

To remove these toxic chemicals and ions, various technologies have been developed including precipitation and co-precipitation, adsorption, coagulation, flocculation, ion exchange, membrane filtration, and solvent extraction technique. However, the major problem associated with these techniques is the use of synthetic toxic reagents that are again non-biodegradable, moreover, these are costly also and thus have high input costs for treatment [32].

Biopolymers, also called natural polymers, are naturally occurring substances generated by living organisms (plants, animals, bacteria, and fungi) [45] throughout their whole life cycle [50].

Due to the following properties, the biopolymers are considered as an attractive alternative to synthetic toxics reagents for the treatment of wastewater:

I. Biopolymers are very abundant as well as cheap.
II. They can be used for the removal of a wide range of contaminants as their adsorption capability can be easily modulated by changing the attached active functional groups, e.g., amino (−NH2) and hydroxyl (−OH) groups.
III. They have diverse applications, in the food, pharmaceutical, and bio-medical industries, attributed to a lot of physical or chemical methods available for their functional modification.

They do not cause any harm to the environment because of their non-toxic, renewable, and biodegradable nature. Only organic wastes like carbon dioxide and water are formed upon biopolymer degradation by naturally occurring microorganisms compared to petroleum-derived plastics having hazardous effects on the environment [32].

Biopolymers can be classified in different ways, for example, based on whether they are natural or synthetic; biodegradable or non-biodegradable; depending on the monomeric units; and source of origin [11, 48] (Figs. 1 and 2 and Table 1).

2 Biopolymers for Wastewater Treatment

Biopolymers being biodegradable and non-toxic substances have been proposed for wastewater treatment owing to their sustainable and renewable properties [30]. Moreover, novel composites with improved properties may be developed by

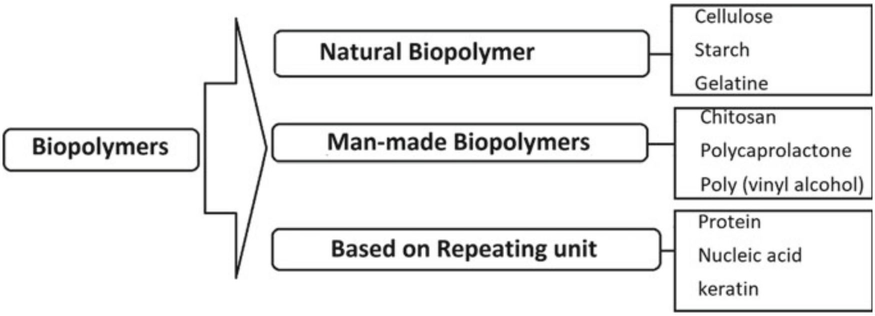


Fig. 1 Biopolymers classification

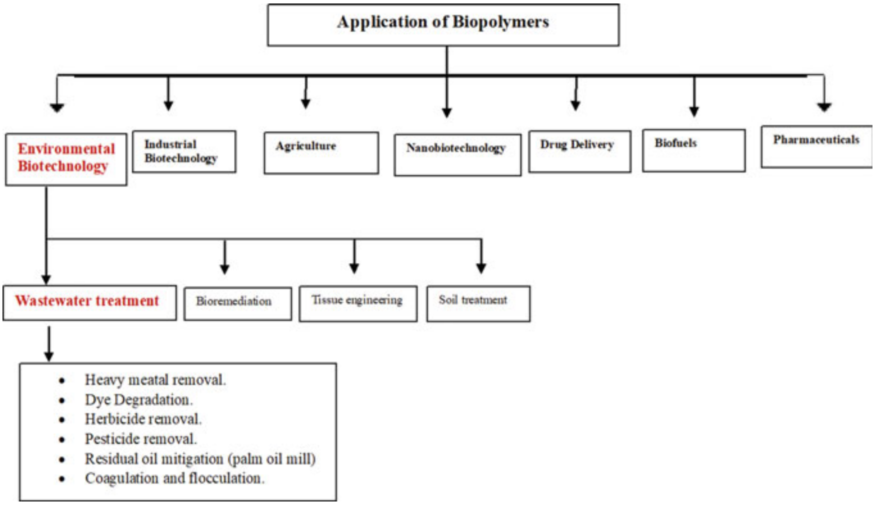


Fig. 2 General application of biopolymers in different fields

grafting biopolymers with various materials such as antioxidants, inorganic nano- or micro-fillers, natural fibres, and pigments [37, 50].

Industrial wastewater contains in large amounts various types of organic and inorganic materials including metals, and hazardous compounds such as fine suspended and dissolved solids. Small particle size and surface charge do not permit finely suspended solids to form heavier aggregates for sedimentation and their removal through filtration is challenging. Residue oil, from Palm oil mill effluent (POME) or vegetable oil mill effluents, is the most important concern in oily wastewaters, and it must be addressed to minimise the formation of interfaces in water-treatment plants, avoid issues in the biological treatment stages, and meet water-discharge criteria. Gravity-based oil separation is challenging and lengthy because emulsified oil droplets do not spontaneously consolidate into bigger flocs [31, 45].

Table 1 Biopolymers and their classification

Biopolymer					
Biodegradable Bio-based			Non-biodegradable		
Microbial origin	Plant origin	Animal origin	Bio-based	Fossil-based	References
Alginate	Cellulose	Chitin/chitosan	Polyethene	Poly (alkylene dicarboxylate)	[15]
Carrageenan	Starch	Nucleic acids	Polypropylene	Poly (glycolic acid)	[49]
Dextran	Polysaccharides	Proteins	Polycarbonate	Polyphosphazenes	[33]
Gellan Gum	Tannin	Glycogen	Polyether amides	Polyvinyl alcohol	[34]
Cellulose	Gums	Glycosaminoglycans	Phenolic resins	Poly caprolactone	[32]

To remove such contaminants from wastewater, a variety of classic and innovative technologies have been used, viz. adsorption, coagulation, precipitation, ion exchange, solvent extraction, membrane filtration, flocculation, and electrolytic and biological processes. Out of these, biopolymers-based adsorption, coagulation, and flocculation are extensively used separation techniques for the removal of heavy toxic metals and compounds, suspended and dissolved particles, and colloids present in industrial wastewater [45]. These are simple and effective wastewater treatment procedures that have a wide range of applications in wastewater treatment [20].

There is an urgent need for the development of technologies that enable the removal of hazardous contaminants from wastewater.

Biosorption is one of the most popular and efficient metal remediation methods. The large number of papers published on the adsorption and remediation of metal ions from aqueous solutions by natural and modified polysaccharides demonstrates a growing interest in biopolymer applications for environmental preservation [12].

In the laboratory, these biopolymers have been successfully tested for pollutant removal from wastewater. Based on the bio-flocculating materials and the wastewater characteristics, these bio-based or microbial flocculants could efficiently lower suspended solids (SS), heavy metals, chemical oxygen demand (COD), total nitrogen content, dye, and turbidity by up to 90% in some situations [35].

Organic polymeric flocculants are currently extensively employed because of their exceptional capability to flocculate effectively at a lower dose [42]. However, it is not preferred due to its non-biodegradability and the dispersion of monomer residues in water, which could pose a health risk. Although synthetic polymers as flocculants have a wide range of applications, their use is contentious because it may have negative environmental and health consequences. The most common hazardous substances, in the case of use of synthetic polymers for wastewater treatment, includes unreacted chemicals such as epi-chlorohydrin, dimethylamine, and formaldehyde that are used to produce the monomers, unreacted residual monomers, like acrylamide, ethyleneimine, and reaction by-products of the polymers in water. Acrylamide is a highly toxic substance that causes severe neurotoxicity. According to the study, cationic poly-electrolytes are more hazardous, especially to aquatic animals, as compared to anionic and non-ionic polymers that are generally less toxic. Furthermore, almost all commercially available polymers are manufactured or processed from petroleum-derived basic components that aren't always safe or environmentally friendly. In addition, these are resistant to biodegradation or their degradation is quite slow, and their degraded monomeric products are still hazardous and have carcinogenic effects upon entering into the food chain. As a reason, the demand for environmentally safe biopolymer-based flocculants, generated from natural sources with effective coagulation properties, is increasing [43].

As a result, scientists all over the world are putting effort to develop these natural flocculants that could potentially replace synthetic flocculants. The challenge now is that natural flocculants are required in large doses due to their low flocculating efficacy and limited shelf life. To generate tailor-made grafted flocculants, synthetic polymers are grafted onto the backbone of natural polymers to combine the best features of both [50].

2.1 Natural Bio-flocculants

As the demand for eco-friendly materials in wastewater treatment has increased in recent years, traditional flocculants have been replaced by bio-flocculants as a feasible alternative. Bio-flocculants derived from natural polysaccharides or other natural polymers such as alginate, cellulose, chitosan, gums, mucilage, and tannins, have attracted researchers' [42] interest as they offer a lot of potential in treatment of wastewater from food and fermentation industry, pharmaceutical industry and cosmetic industry.

Bio-flocculants' mode of action of pollutant removal involves destabilisation of colloidal particles by an increase in the ionic strength that results in a decrease in zeta potential and, consequently, a thinner diffuse section of the double electrical layer. Alternatively, these polymers may selectively absorb counterions to neutralise the charge of particles and thus interact with pollutants due to the presence of diverse functional (carboxyl or hydroxyl) groups in their macromolecular structures [18].

2.1.1 Mode of Action for Natural Bio-flocculants

The natural polymer chitosan's depolluting activity depends on its cationic nature, due to reactive functional groups like amino groups and/or hydroxyl groups and a large molecular weight that can lead to charge neutralisation by coagulation and flocculation of pollutants by bridging mechanisms.

According to a study that examined chitosan's coagulation and flocculation potential for dye removal from the solution, it was revealed that protonated amine groups from chitosan electrostatically attract the anionic dye resulting in charges neutralisation, and further, the flocculation was enhanced leading to agglomerates binding with each other and settling by the bridging mechanism [18].

Many factors influence chitosan's activity to form hydrogen bridges or for hydrophobic interactions like the nature of the colloids, its molecular weight and level of deacetylation, pH of the suspension, and its dosage. For other natural polymers that are anionic, for example, cellulose, or tannin, they also require the help of cations to flocculate anionic contaminants from wastewater. Thus, cationic polymers such as chitosan or inorganic metal salts (aluminium or ferric salts) are added for charge neutralisation of negatively charged contaminants before the addition of anionic natural flocculants. After neutralisation of charge, anionic cellulose, sodium alginate or tannin with a negatively charged backbone allowed the polymer extension in solution and created loops and tails to aid bridging of flocs [50].

It's worth noting that most plant-based bio-flocculants, for example, that are anionic or non-ionic can be utilised directly in wastewater treatment without any coagulants' help. One such study investigating the flocculation potential of *Plantago psyllium* mucilage and *Tamarindus indica* mucilage for textile wastewater concluded polymer bridging as a probable flocculation mechanism. The flocculation process of other plant-based bio-flocculants like Mallow and Tamarind mucilage could not be predicted if the surface charge is not known [18].

2.2 Grafted Flocculants/Graft Copolymers

Graft copolymers for wastewater flocculation have been developed in response to the growing market demand for efficient and cost-effective flocculants in wastewater treatment. Grafted copolymers have thus evolved as novel materials with enormous potential for wastewater treatment due to their unique characteristics and higher performance over conventional polymeric flocculants. Natural polysaccharides have been modified to combine their best characteristics with existing synthetic polymers and hence improve the flocculation ability by increasing the percentage of effective constituent and positive electric charge of the flocculants [47]. Polysaccharides, unlike long-chain synthetic polymers, are relatively shear stable and biodegradable. However, because of their poor efficiency, greater concentrations or dosages are required. It is apparent that irrespective of natural or synthetic nature, all polymers have some disadvantages. By grafting synthetic polymers onto the backbone of natural biopolymers, numerous attempts have been made to combine the best features of each. Some examples of grafted flocculants include polyacrylamide grafted-starch, polyacrylamide grafted-hydroxypropyl methylcellulose, polyacrylamide grafted-carboxymethyl guar gum, polymethylmethacrylate grafted -psyllium, and poly (2-hydroxyethyl methacrylate) grafted -agar [47]. The flocculating property of these copolymers has been successfully investigated in kaolin suspension (synthetic wastewater) by the Jar test method suggesting that these flocculants might be used in commercial wastewater treatment. Many more copolymers have been effectively produced by grafting polyacrylamide or polytrimethyl ammonium chloride chains onto natural biopolymers like agar, celluloses, chitosan, gums, sodium alginate, starches, and oatmeal [45]. The flocculating capabilities of these have been tested in a variety of wastewater effluents (e.g., municipal sewage effluent, pulp mill effluents, raw mine wastewater, and textile effluent). The experiments revealed that flocculating efficiency of grafted copolymers in an aqueous solution is dependent on their molecular extensions. Thus, by varying the length and number of grafted polyacrylamide chains, graft copolymers' efficiency can be modulated. It was found that graft copolymers with high molecular weight and branching status are more efficient flocculating agents even at a lower dose. The occurrence of grafted polyacrylamide chains also increased the hydrodynamic volume (i.e., the radius of gyration) of a polymer in solution, improving its flocculation capacity, according to the simple approachability model of flocculation. Studies have also shown that graft copolymers are better in turbidity removal as compared to commercially available flocculants. Grafting alters the structure of natural polysaccharide molecules, making it less appropriate as a substrate for enzymatic breakdown and is reported to be less vulnerable to biodegradation. Furthermore, grafting polysaccharides enhances the inert polyacrylamide content, making it less susceptible to biological attack and more resistant to biodegradation. Grafting shear degradable polymers onto the rigid polysaccharide backbone also results in systems that are relatively shear stable. Cationic organic flocculants are more effective in removing negatively charged pollutants or particle suspensions such as clay and dye. Consequently, grafted cationic flocculants have been produced by combining a cationic moiety N-(3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) with the guar gum or starch backbone in the presence of sodium hydroxide. These CHPTAC-based cationic flocculants showed better flocculation performance to remove negatively charged particles in suspension as against commercially available flocculants. However, a certain type of wastewaters like textile effluent is more complex and may contain both unwanted cationic and anionic colloidal particles. As a result, amphoteric flocculants containing both cationic and anionic ions were proposed to remove both cationic and anionic pollutants. Chitosan-based amphoteric flocculants have been produced in recent years, and their flocculating properties have been assessed in kaolin suspension, raw river water, and dye-containing solution. In comparison to chitosan alone, amphoteric chitosan copolymer exhibited greater removal potential and formed noticeably more compacted flocs. In a nutshell, grafting is a very efficient method of modulating the characteristics of polysaccharides so that they can be “tailor-made” to meet specific requirements and make highly efficient graft copolymers. However, the absence of commercial production methods remains the major challenge with graft copolymers. The most common ways to make grafted polysaccharides involve the use of chemical-free radical initiators, i.e., the conventional approach, high-energy X-ray and gamma radiations, UV-radiation-based procedures, and microwave-based methods. In the conventional approach, a chemical-free radical initiator such as ceric ammonium nitrate (CAN) is used to generate free radical sites on the backbone polymer, where the graft monomer is added up to form the graft chain. This method of synthesis is not suited for large-scale industrial applications due to its limited reproducibility.

The use of high-energy radiation as the free radical initiators is a better way of graft copolymer production, but this method can damage the polysaccharide backbone by the process of radiolysis. The UV radiation approach requiring the presence of a photosensitiser can also be utilised, but due to the poor penetration of UV radiation, it is only suited for surface grafting. The best approach for graft copolymer synthesis until now is to use microwave radiation to produce free radical sites on the backbone polymer, however, this method has a high input cost. In conclusion, more studies are needed to find an ecologically friendly and economically viable approach for producing high-quality grafted flocculants with outstanding pollutant removal capabilities, and these modified products can be used to treat a variety of industrial effluents [18].

2.2.1 The Mechanism for Grafted Flocculants/Copolymers

Grafted flocculants or copolymers utilise charge neutralisation and polymer bridging as a flocculation mechanism for wastewater treatment. At the start of the flocculation process, charge neutralisation predominates, resulting in the rapid production of a large number of insoluble complexes. The insoluble compounds then combine and form bigger net-like flocs due to the bridging effect of the flexible polymeric graft chains. Finally, the compacted flocs are generated that settle quickly. Other studies suggested polymer bridging as the dominant flocculation mechanism [1]. The reason that graft copolymers have greater flocculation qualities than linear polymers is related to the polymer bridging mechanism. Polymer chain segments get adsorbed onto the surfaces of distinct particles, bridging and linking all the nearby particles. Due to the longer polymeric chain of grafted flocculants and greater gyration radius, the adsorbed polymers tend to assume a more stretched structure thus interacting with multiple particles [49].

3 Polysaccharide-Based Products for Wastewater Treatment

Polysaccharides are polymers of carbohydrates, in which monosaccharides (for example, cellulose, chitosan, glycogen, and starch) join through glycosidic linkages to form long linear chains [50]. Polysaccharides are hydrolysed to produce monosaccharides or oligosaccharides [11]. These have gained attention as bio-based flocculants in drinking-water and wastewater treatment attributed to their unique properties, including accessibility, biodegradability, and structural characteristics that facilitate functional modifications [23, 42] (Fig. 3).

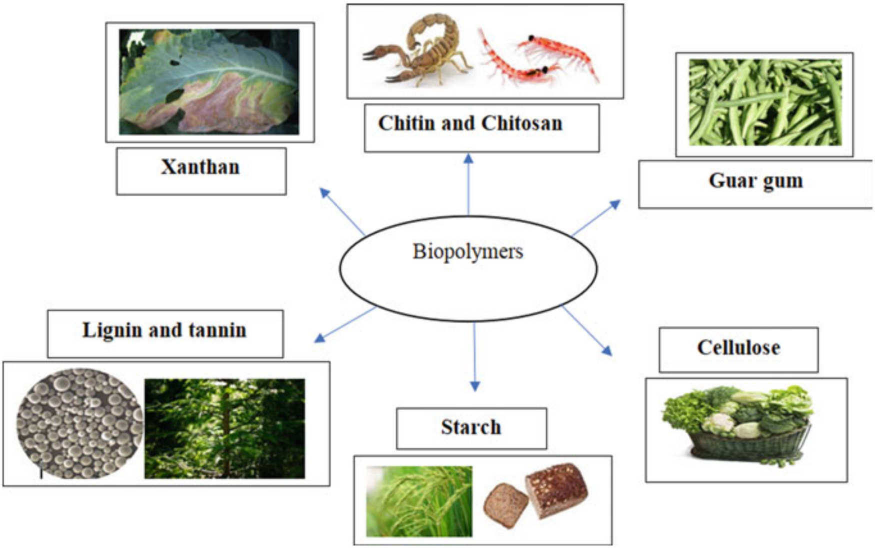


Fig. 3 Polysaccharide-based products for wastewater treatment

3.1 Chitosan

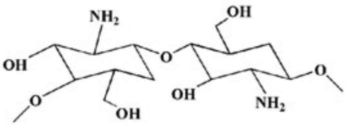
Chitosan is a linear polysaccharide comprising monomeric units of N-glucosamine (deacetylated) and N-acetyl-D glucosamine linked through β-1, 4 glycosidic bonds [5]. The order and distribution of the two monomers along the chain determine their physical, chemical, and biological properties [28]. It is obtained by deacetylation of chitin, a natural biopolymer found in exoskeletons of crustaceans, shellfish, arthropods, fungi cell walls, and insects [32]. Chitin and chitosan, being biodegradable and non-toxic, have diverse applications. As chitosan produces hydrocolloid and causes gelling of water, it can be utilised as food additives, thickening agents, and coating agents in the food industry. In cosmetics, it is used to make skin-care products and creams [5]. Chitosan is also employed in drug delivery systems, for enzymes and microbial cell immobilisation. It can be used as a biocontrol agent for handling plants diseases. It may be used for making porous materials for bioreactors [30].

Since chitosan is a polycationic macromolecule, it can be a promising flocculant as most natural colloids are negatively charged. Chitosan is insoluble in water and organic solvents. But it is soluble in dilute organic acids (like acetic and formic acid) and inorganic acids, due to the protonation of the free amino groups [28]. In acidic solutions ($pH < 5$), chitosan transforms into a soluble cationic polymer with a high charge density that can electrostatically interact with negatively charged contaminants, such as metal anions, dyes, and organic compounds, present in wastewater. Owing to its adsorption properties, it can also be for the removal of suspended and dissolved solids [28].

Different chitosan-based products such as films, nanofibers, powder, and beads have been generated through various physical modifications [38, 9, 3, 17]. Chitosan-based biocomposites have recently been developed, to overcome chitosan's limitations and provide physical strength and magnetism [8, 19]. Further, scientists have produced chitosan nanofibers with adjustable pore sizes and large specific surface areas [19, 10]. Pure chitosan nanofiber membranes (129 nm diameter) developed by the electrospinning technique could be used for as Vanadium (V) removal from water [25]. Likewise, chitosan-polyvinyl alcohol or zeolite nanofiber composite has been developed by blending and electrospinning technique [9]. Such nanofiber composites are reusable up to five times and are stable at various pH [27].

Chemically modified chitosan derivatives have superior adsorption capacity, mechanical resistance, and chemical stability [32]. Many studies have successfully evaluated its flocculation and coagulation properties for dye removal, organic matter (e.g., lignin and chlorinated compounds), heavy metals, and phenolic compounds removal in textile, pulp and paper mill, and cardboard-mill wastewater [18] (Table 2).

Table 2 Chitins and Chitosans' potential in pollutants' removal

<table>
<tr><td colspan="4">Chitin and Chitosan
</td></tr>
<tr><td>Sources</td><td>Products</td><td>Applications</td><td>References</td></tr>
<tr><td rowspan="7">
crab

Scorpions

Crustaceans

Locust</td><td>Chitosan Particles, Aerogels, Composites</td><td>Dyes and Metals removal</td><td>(Russo <i>et al.</i>, 2021)</td></tr>
<tr><td>Water-soluble flocculants and Nano sorbents</td><td>Organic pollutants/Oil</td><td>(Jacob and Gopi, 2021)</td></tr>
<tr><td>Beads</td><td>Drug/emerging pollutants</td><td>(Sarode <i>et al.</i>, no date)</td></tr>
<tr><td>Carboxylated chitosan/Fe3O4</td><td>Fluoride, nitrate and phosphate removal</td><td>(Pandey, 2020)</td></tr>
<tr><td>Chitosan solution</td><td>Turbidity and TDS removal</td><td>(No and Meyers, 2000)</td></tr>
<tr><td>Carboxy methyl chitosan-graft-polyacrylamide (CMC-g-PAM)</td><td>Dye removal</td><td></td></tr>
<tr><td>Carboxy methyl chitosan-g-poly(2-methacryloyloxyethyl) trimethyl ammonium chloride</td><td>Dye removal</td><td>(Chen <i>et al.</i>, 2020)</td></tr>
</table>

(continued)

Table 2 (continued)

 fungi  Starfish	**(CMC-g-PDMC)**		
	Chitosan grafted copolymer of acrylamide and 3-acrylamide propyl trimethylammonium chloride **(CTS-g-PAA)**	Dye removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
	Chitosan-acrylamide-fulvic acid **(CAMFA)**	Colour removal	(Zubair and Ullah, 2021)
	Amphoteric carboxy methyl chitosan **(CMC-CTA)**	Turbidity removal	(Maćczak *et al.*, 2020)
	Carboxylated chitosan-graft-polyacrylamide co-sodium xanthate	Turbidity removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
	Carboxylated chitosan-graft-poly (acrylamide-2-acrylamido-2-methylpropane sulfonic acid (CPCTS-g-P(AM-AMPS)	Heavy metal removal	(Pal *et al.*, 2021)
	Chitosan graft-poly (acrylamide-acryloyloxyethyl) trimethylammonium chloride (CS-g-PAD)	Zinc phosphate removal	(Yue *et al.*, 2019)

3.2 Gums and Mucilage

Plant-based gums and mucilages have emerged as an environment-friendly green technology for wastewater treatment and have been endorsed as a safer and valuable alternative to existing traditional inorganic coagulants [32]. The common plant species as a source of gums, that have been used to develop flocculants, includes Hibiscus (Okra), *Malva sylvestris* (Mallow), *Plantago psyllium* (Psyllium), *Plantago ovata* (Isabgol), *Tamarindus indica* (Tamarind), and *Trigonella foenum-graecum* (Fenugreek) [51]. Aqueous extraction, alcohol precipitation, and drying are the most common methods for obtaining plant-based flocculants [27].

They have demonstrated promising results for the removal of COD, colour, total suspended solids, and turbidity, in the treatment of landfill leachate, effluents from textile, tannery, and sewage. In terms of treatment efficiency, some plant-based gums showed equivalent efficacy to synthetic flocculants even at low concentrations. Okra gum (0.12 mg/L) and Fenugreek mucilage (0.08 mg/L) were able to remove >85% of suspended particles from sewage wastewater and tannery effluent, which is comparable to synthetic polyacrylamide [27].

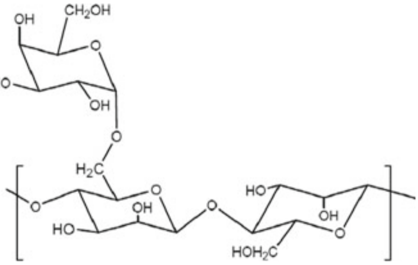
A gum xanthan-psyllium-cl-poly (acrylic acid-co-itaconic acid)-based adsorbent has been successfully tested to remove the dyes such as Auramine O (Aur-O) and Eriochrome black T (EBT) from the aqueous solutions and is also recyclable with less reduction in activity up to six and three cycles, respectively [4]. Likewise, grafted binary psyllium (Psy-g-Poly) was recently produced and evaluated for Hg (II) ion removal from an aqueous solution. Even at a high concentration of Hg (II) ions (100 ppm), the adsorbent showed a great (approx. 96%) adsorption effectiveness [32] (Table 3).

3.3 Cellulose

Cellulose, one of the most abundant natural fibrous polysaccharides, is a linear chain polymer of β-1, 4 linked D-glucopyranose and is obtained mainly from wood sources and cotton [32]. Even though the applications of pure cellulose are very limited, modifying its physical and chemical properties, for example, direct chemical modification of hydroxyl groups of cellulose by various agents, has recently received great attention to improving its industrial applications. The chemically modified cellulose or its derivatives can be obtained either by incorporating chelating or metal binding functional groups directly into the cellulose [39] or alternatively, grafting the monomers to cellulose [51].

Etherification, esterification, oxidation, and halogenation are the most common cellulose functionalisation processes [32]. The chemically modified cellulose shows improved adsorption for heavy metals in aqueous and non-aqueous solution and also exhibits altered properties like hydrophobicity or hydrophilicity, elasticity, microbiological, heat, and mechanical resistance [29, 24]. Cellulosic materials have numerous

Table 3 Gum-based products and their applications for wastewater treatment

Guar gum 			
Sources	**Products**	**Applications**	**References**
 guar beans	**HPTAC-guar** (Hydroxyl propyltriammonium chloride guar gum)	COD Removal, turbidity removal and biological Contaminants removal from municipal wastewater	(Russo *et al.*, 2021)
	CGG (cationized guar gum)	Bentonite aggregation	(Jacob and Gopi, 2021)

applications ranging from medical, pharmaceutical, cosmetics, energy storage materials to nanocomposites, membranes, and barrier films, as well as electronics, sensors, and supercapacitors [27].

Anionic sodium carboxymethyl-cellulose (CMCNa) produced from date palm rachis, an anionic water-soluble polyelectrolyte that is renewable, non-toxic, and biodegradable, has been explored as an environment-friendly flocculant for turbidity removal in drinking water treatment, together with aluminium sulphate (as a coagulant). Another study tested the flocculating performance of ionised Dicarboxylic acid nano-cellulose (DCC) flocculant (with ferric sulphate as a coagulant) in municipal wastewater. Nanofibrils cellulose (NFC) and cellulose nanocrystals (CNCs) have recently gained significant attention as Nano-sorbents because of their unique features and are examined for wastewater treatment. Although various studies highlighted the efficacy of cellulose-based nanomaterials in the removal of different contaminants, their environmental consequences, as well as their non-toxicity and biodegradability characteristics, still need to be evaluated [29].

3.3.1 Membranes for Water Treatment

Cellulose-based nanofibers (CNF) or cellulose microfibres have been used for the development of biocomposite membranes with CNF embedded in a polymer matrix (cellulose triacetate, poly-pyrrole, poly-(ether sulfone), poly-(acrylonitrile), poly-(ethylene oxide), poly-(vinyl alcohol), poly-(vinylidene fluoride), and poly-(3-hydroxybutyrate)). These biocomposite-based membranes, created from fibre-reinforced biopolymers, have been tested for distillation, haemodialysis, and filtration [18].

3.3.2 Different Chemical Treatments

Recently, various chemical treatments have been used to modify the surface of cellulose-based nanomaterials to improve their affinity for hydrophobic materials and the removal of organic pollutants.

Microbial cellulose surfaces coated with TiO2 (MC/TiO2) have been used to degrade toluene in air at room temperature when exposed to UV light [36]. Likewise, cellulose nanofiber (CNF) aerogels coated with triethoxyl (octyl) silane, by vapour phase deposition method, resulted in the production of reusable hydrophobic materials having a strong affinity to oils and thus improved sorption efficiency for organic solvents. Wang et al. [44] evaluated the Nano-cellulose-based hydrogels that were modified with graphene oxide for sorption of cyclo-hexane and dimethyl-formamide (DMF).

Reusable sponge-like (micro- or Nano-sized) systems have been created, by thermal crosslinking of (2, 2, 6, 6-Tetra-methylpiperidin-1-oxyl) (TEMPO)-oxidised cellulose nanofibers (TOCNF), citric acid, and branched poly-ethylene-imine (bPEI), with improved adsorbent efficacy for diverse dyes, for example, Brilliant Blue R, Cibacron Brilliant Yellow, and Naphthol Blue Black [51].

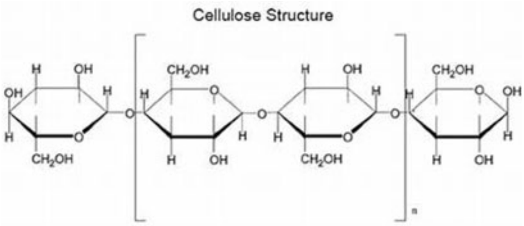
Crosslinking the self-assembled TO-CNF with Tri-methylolpropane-tris-(2-methyl-1-aziridine) propionate (TMPTAP) and poly-ethylene-imine (PEI) had efficient Cu (II) adsorption capability [18]. A study demonstrated that nano-cellulose-based aerogels/fibres with a very thin layer of TiO2 nanoparticles (low-energy surface layer) had improved with oleophilic and hydrophobic properties and thus can be used for oil and organic solvent removal from water [12].

Another study evaluated and compared the dye and heavy metal adsorption abilities of lignocellulose-based materials, before and after physical and chemical treatment and concluded that altering their physical and chemical properties improves their qualities and expands their industrial applications [51]. Anionic sodium carboxymethyl cellulose (CMC Na), made from date palm rachis waste, was investigated as an environment-friendly flocculant for removing turbidity in drinking water treatment, together with aluminium sulphate as a coagulant [27].

Another study created an ionised dicarboxylic acid nano-cellulose (DCC) flocculant and tested its flocculating potential in municipal wastewater using ferric sulphate as a coagulant [45] (Table 4).

Table 4 Cellulose-based products and their applications in wastewater treatment

Cellulose



Sources	**Products**	**Applications**	**References**
 Fibre which vegetable  Sugarcane  Cotton	Anionic cellulose	Textile effluent treatment	(Olivera *et al.*, 2016)
	Cationic cellulose	Colour removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
	Quaternized-cellulose **(QC)**	Anionic dyes removal	(Yue *et al.*, 2019)
	Aerogels, fibres, membranes	Organic pollutants/oil, heavy metals Removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
	Hydroxy-propyl methyl cellulose grafted with polyacrylamide **(HPMC-g-PAM)**	Kaolin and iron-ore suspension Clarification	(Asif *et al.*, 2021)
	Sodium- carboxy methyl cellulose (**CMCNa**) and Carboxymethyl cellulose-g-polyacrylamide (**CMC-g-PA**)	Turbidity removal from drinking water and Clarification of Kaolin suspension, respectively	(Zubair and Ullah, 2021)

(continued)

Table 4 (continued)

	Nano-sorbents and Nanostructured materials	Dye and Heavy metals Removal	(Maćczak *et al.*, 2020)
	Dicarboxylic acid nanocellulose (**DCC**)	Turbidity removal and Municipal wastewater treatment	(Pandey, 2020)
	Cationic cellulose nanofibers (**CCNF**)	Pulp slurry flocculation	(Jacob and Gopi, 2021)
	Poly acryloyloxy ethyl trimethyl ammonium chloride-g-cellulose nanocrystal **(PAETMAC-g-CNC)**	Colour Removal.	(Olivera *et al.*, 2016)
	3 anionic sulfonated nanocellulose **(ADAC)**	Turbidity and COD removal	(Maji and Maiti, 2021)
	Grafted microcrystalline cellulose MCC (pAA-co-pDMC)	Turbidity and Colour removal	(Zhao *et al.*, 2020)

4 Other Polysaccharides

Other polysaccharides-based polymers like alginate, lignin, and starch have also been tested for wastewater treatment. For example, grafted copolymer of starch with acrylamide and dimethyl-diallyl ammonium chloride was reported for the wastewater treatment from textile effluent. In comparison to a traditional coagulation-flocculation procedure, this composite coagulant reduced the requirement of chemical dose by more than 50% [2, 11].

4.1 Starch

Starch is a key energy source that is made up of grain products in the proportions of 60% to 75% by weight [49]. It consumes between 70 and 80 per cent of the calories produced by the human body or living thing [27]. Typically, starch-based products are added to alter the physical qualities of food, and they have a variety of applications including thickening agent, adhesive, and moisture retention material [11, 49] (Table 5).

4.2 Tannin

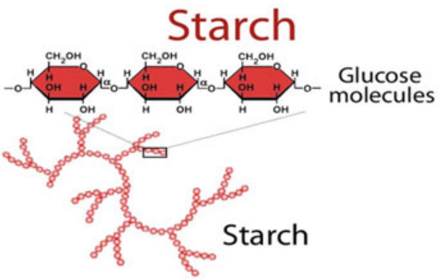
Tannins are secondary metabolites and anionic polymers found in fruits, leaves, and bark and are biodegradable in nature [32]. Their flocculating ability has been studied for removing various pollutants found in drinking water as well as wastewater, for example, suspended, colloidal materials, dyes, inks, and pigments. During the process, first a coagulant such as aluminium sulphate neutralize the negative charge making colloidal particles unstable, while anionic tannin acts as a flocculant to link the destabilised aggregates together to create flocs large enough to sediment. The study proved that combining aluminium sulphate (used as a coagulant) with tannin (used as a flocculant) considerably decreased the amount of coagulant required for treatment. Modified tannin (Tan floc flocculant) overcomes the need for coagulant for the treatment and has recently been evaluated for heavy metals removal with high efficiency from polluted surface water and municipal wastewater. Tan floc is manufactured from *Acacia Mearnsii* bark that has undergone physio-chemical modifications that impart cationic characteristic. The chemical change includes the addition of a range of hydrocolloid gums and soluble salts containing substituted amino sites in the structure. Owing to its cationic characteristic, direct flocculation was achieved without the need for any coagulant or pH correction [45, 48].

A novel adsorbent poly (tannin-hexa-methylene-diamine) (PTHA), produced by the one-pot green synthesis method, was evaluated for Cr (VI) exclusion from water by changing the molar ratio of tannin and hexa-methylene-diamine. Further, by using tannin grafted on cellulose (TM) microfibers, the cationic dye was successfully removed from the aqueous solution recently [32] (Table 6).

4.3 Alginates

Alginate is a heteropolysaccharide made up of 1 → 4-linked-β-d-mannuronic (MA) and 1 → 4-linked α-guluronic acid monomers (GA) [16]. Stanford was the first to isolate it in 1881. In nature, alginate is found as salts of calcium, magnesium, and sodium with alginic acid and is present in a variety of species of Phaeophycean,

Table 5 Starch-based products and their application in wastewater treatment

<table>
<tr><td colspan="4">Starch
 </td></tr>
<tr><td>Sources</td><td>Products</td><td>Applications</td><td>References</td></tr>
<tr><td rowspan="5">
Sushi rice

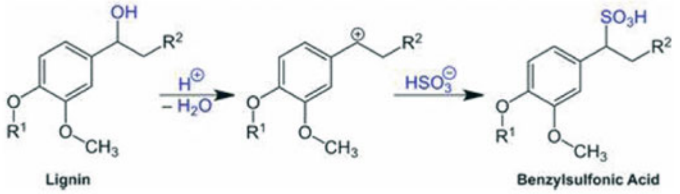
Raw oats

Pumpernickel bread</td><td>Cationic starch</td><td>Turbidity removal from kaolin suspension, bentonite clay and natural clay</td><td>(Russo <i>et al.</i>, 2021).</td></tr>
<tr><td>Dispersible-cationic starch (DCS)</td><td>Clarification of Kaolin suspensions</td><td>(Nasrollahzadeh <i>et al.</i>, 2021)</td></tr>
<tr><td>(2-hydroxypropyl) trimethyl-ammonium chloride etherified carboxy-methyl starch (CMS-CTA)</td><td>Clarification of kaolin and hematite suspension</td><td>(Schmidt, Kowalczyk and Zielinska, 2021)</td></tr>
<tr><td>Polyacrylamide grafted starch (St-g-PAM)</td><td>Clarification of kaolin suspension</td><td>(Maćczak <i>et al.</i>, 2020)</td></tr>
<tr><td>Hydroxyethyl starch-grafted poly (N, N dimethyl-acrylamide-co-acrylamide) HES-g-poly-(DMA-co-AM)</td><td>Metal ions and dye removal</td><td>(Zhao <i>et al.</i>, 2020)</td></tr>
</table>

i.e., brown seaweed. *A. nodosum, L. hyperborean, M. pyrifera, and S. japonica* are used to produce commercial alginates. Alginates of bacterial origins have also been documented; however, this type of alginate is not yet commercially available. Alginate extraction is a relatively simple procedure that has been well documented in the literature [6, 18, 42].

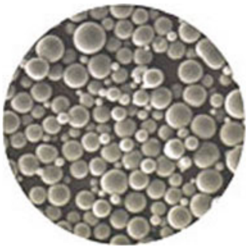
These have robust metal ion chelating properties owing to the occurrence of several functional groups like hydroxyl (–OH), carboxylic (–COOH), and oxo/carbonyl

Table 6 Applications of Lignin- and Tannin-based polymers for wastewater treatments. *Source* [37]

<table>
<tr><th colspan="4">Lignin and tannin
 </th></tr>
<tr><th>Sources</th><th>Products</th><th>Applications</th><th>References</th></tr>
<tr><td rowspan="5">lignin</td><td>Kraft lignin copolymer (KLD)</td><td>Turbidity removal</td><td>(Pandey, 2020)</td></tr>
<tr><td>Sulfo-methylated softwood kraft lignin (OSKL)</td><td>Cationic dye removal</td><td>(*Lee et al., 2014*)</td></tr>
<tr><td>Tannin</td><td>Turbidity removal</td><td>(Zhang *et al.*, 2017)</td></tr>
<tr><td>Tanfloc (plant-derived modified tannin)</td><td>Heavy metal removal</td><td>(Wang *et al.*, 2021)</td></tr>
<tr><td>A-TN, Q-TN (modified larch tannin and its quaternized derivative)</td><td>Algal water treatment</td><td>(Jacob and Gopi, 2021)</td></tr>
</table>

(C=O) groups. Sodium alginate is a linear water-soluble anionic polymer (500,000 average molecular weight) that has been investigated for its flocculating efficiency for textile wastewater treatment and synthetic colour removal, with aluminium sulphate used as a coagulant [27]. The findings of the experiments showed that it has great flocculating potential, and treatment leads to colour removal (>90%) and COD reduction (80%) [18]. Because of its benign nature, durability, biodegradability, and water permeability, alginate is widely used in wastewater remediation for pollutant adsorption [13, 16] (Table 7).

Table 7 Metal ion sorption properties of alginate-based products

Source	Alginate-based products	Adsorbent Metals	References
	Carboxylated alginic acid	Cu (II), Pb (II)	(Nasrollahzadeh *et al.*, 2021)
	Alginate beads	Cu (II), Cd (II), Pb (II)	(Fertah *et al.*, 2017)
	Alginate capsules, Alginate coated gel	Pb (II)	(Shaikh *et al.*, 2021)
	Hybrid beads of sodium alginate with chitosan microspheres	Pb (II), Cr (VI)	(Russo *et al.*, 2021)

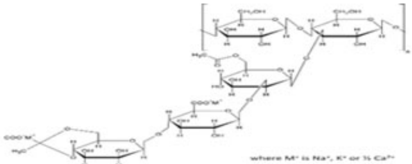
4.4 Xanthan

Xanthan gum, a complex copolymer produced by a bacterium, i.e., *Xanthomonas campestris*, was one of the first commercially effective bacterial polysaccharides to be developed through fermentation [21]. Xanthan is a polymer with five distinct sugar groups as “repeat units”. It’s widely utilised in both the food and non-food industries [14].

Xanthan and other natural gums have been suggested as a safer substitute to industrial flocculants in wastewater treatment [21]. *Xanthomonas campestris* ferments carbohydrates to produce hydrocolloids, which includes glucose, mannose, and glucuronic acid, as well as partially esterified acetic and pyruvic acids [30, 51].

Xanthated chitosan has been investigated to reduce the Cu (II) ions in kaolin suspensions. Further, a free radical-mediated grafting process in an inert environment was used for the production of polyacrylamide grafted xanthan gum/silica (XG-g-PAM/SiO2) [21] that has been explored to reduce the turbidity in kaolin- and iron ore-suspensions [27]. In a study, novel hybrid nanocomposites were prepared, by introducing silica nanoparticles into the graft copolymer by hydrolysis and condensation of Tetra-ethyl-ortho-silicate (TEOS), and its flocculation properties were successfully tested for turbidity removal from effluent in a dose-dependent manner [23] (Table 8).

Table 8 Xanthan-based products and its application in wastewater treatment

Xanthan 			
Source	**Products**	**Applications**	**References**
	Polyacrylamide grafted xanthan gum/silica (XG-g-PAM/SiO2)	Turbidity removal	(Russo *et al.*, 2021)
	Tetra ethyl ortho silicate (TEOS).	Iron metal removal	(Maji and Maiti, 2021)
	Xanthated chitosan	Cu(II) ions removal	(Pal *et al.*, 2016)

4.5 Pullulan

Some studies have evaluated the pesticide-flocculation properties of pullulan or its derivatives in wastewater. The pullulan can be modified to contain pendant tertiary amine or quaternary ammonium salts. Ghimici and co-workers based on UV/Visible spectroscopy analysis revealed strong interaction of pesticide particles with polycations resulting in efficient, about 80–98%, pollutant removal. Moreover, zeta potential measurements verified charge neutralisation as the main flocculation mechanism but chelation and hydrogen bonding can also be the probable flocculation mechanism.

5 Advantages and Limitations of Using Polysaccharide-Based Products for Metal Ion Adsorption

5.1 Advantages of Natural-/Biopolymers

In comparison to typically used sorbents, such as activated carbon and synthetic ion-exchange resins, for removing metal ions from aqueous solutions, polysaccharide biopolymers have many advantages:

- These are economic and are derived from natural raw resources as compared to the majority of commercially available petroleum-based polymers and ion-exchange resins that are non-safe and detrimental to the environment. Because of this reason, naturally derived low-cost alternatives are gaining popularity over synthetic polymers.
- Polysaccharide bio-sorbents are incredibly cost-effective to utilise since they are easy to prepare quality crosslinked materials from low-cost reagents and also have minimal operational and maintenance costs. While the activated carbon and ion-exchange resins are very costly, increasing the quality increases the input cost [46].
- Because of the versatile nature of the materials in terms of variable structure and properties, bio-sorbents can have multifunctional applications, including the use as insoluble beads, gels, films, membranes, and filters.
- Polysaccharide-based sorbents have a high capacity, high rate of adsorption, and thus are very efficient at removing pollutants at various concentrations. They can also be modified for removing selective pollutants present in solution either at very low or high concentrations [2, 46].
- The modification of functional groups of polysaccharide-based biopolymers can enhance their chelating properties for a large number of contaminants such as dyes, aromatic compounds, and several metal ions.
- The amphiphilic property of crosslinked biopolymers like cyclo-dextrin polymers makes them attractive since they are sufficiently hydrophilic to swell in water, allowing the adsorbate to diffuse quickly, while still possessing extremely hydrophobic sites that easily trap nonpolar contaminants. Activated carbons on the other hand have a poor adsorbing capacity of certain hydrophilic compounds and metal ions [2].

5.2 Limitations of Natural Adsorbents

The absence of efficient extraction and purification techniques is the primary barrier to the development of these polysaccharides. The drawbacks to employing polysaccharides in wastewater treatment can be summed up as follows:

- The adsorption qualities of natural polymers are determined by the raw materials used. The adsorption ability of chitin- and chitosan-based products is affected by the polysaccharide's origin, degree of acetylation and deacetylation, molecular weight, solution characteristics, water affinity, and amino group concentration. These variables influence the polysaccharide's swelling and diffusion properties, as well as its characteristics. These difficulties, along with chemical heterogeneity, may explain why scaling up polysaccharide-based products from the laboratory to the industrial scale is problematic.
- Any polysaccharide system must account for the extreme variability of industrial and municipal wastewaters in its design. Each sort of contaminant could

require a different polysaccharide. Each polysaccharide appears to have a unique application in wastewater treatment, as well as inherent benefits and drawbacks. Heavy metal ions have a strong affinity for chitosan-based compounds. The ability of cyclodextrin sorbents to form inclusion complexes with organic molecules, particularly aromatics, is exceptional, but their metal affinity is very weak [46].

- The type of material chosen has a significant impact on performance. The degree of chemical activation and modification determines the adsorption characteristics. The ideal approach for accomplishing selective extraction of chitosan is to utilise a metal-specific ligand but finding a specific ligand for each metal ion has proven impossible.
- Adsorption efficiency is determined by physio-chemical features of sorbents such as porosity and specific surface area. Another issue with insoluble polysaccharide-based materials is that they have poor physio-chemical properties, particularly in terms of porosity. In general, polysaccharides are nonporous and their derivatives have a low specific surface area. Dried pectin compounds, such as sugar beet pulp, have a low specific surface area of about 5 m^2/g, but their hydration and water retention ability allow them to achieve a specific surface area of about 300 m^2/g. Likewise, chitosan also has a low specific area, which ranges from 2 to 30 m^2/g. The specific surface area of glutaraldehyde-crosslinked chitosan beads, epichlorohydrin-cyclodextrin gels, and epichlorohydrin starch beads is 60, 213 and 350 m^2/g, while most commercial activated carbons, on the other hand, have a high specific surface area between 800 and 2000 m^2/g.
- The performance of the system is determined by the parameters of the wastewater. The complexation of metal ions is highly influenced by pH. The pH of the wastewater plays a significant role in the speciation of metallic ions. Furthermore, under strongly acidic conditions, the chitosan beads' amine groups easily create protonated groups, which cause metal ions to repel each other electrostatically. Protons and metal ions compete for adsorption sites because of protonation.

6 Protein-Derived Materials for Wastewater Treatment

Just like others, protein-based products because of their distinctive properties, such as natural abundance, biodegradability, non-ecotoxicity, and ease of modification due to the existence of many functional groups, have got dramatic attention over the last two decades. Proteins are intriguing options for wastewater treatment because of their unique features. Polymeric proteins like albumin, gelatine, keratin, soy, and silk proteins have been explored for industrial wastewater treatment [51] (Table 9).

Table 9 Protein-derived materials for wastewater treatment

Sources	Products	Applications	References
	Silk proteins	Industrial wastewater treatment	(Russo *et al.*, 2021)
	albumin		(Martins *et al.,* 2008)
	keratin		(Zubair and Ullah, 2021)
	Soybean derived proteins		(Jacob and Gopi, 2021)

7 Challenges

Although biopolymers-based flocculants showed notable potential in wastewater treatment, there are still many challenges that need to be overcome. Natural polymers have a lower shelf life than synthetic polymers because their active components deteriorate over time and must be properly regulated [26]. Furthermore, due to their biodegradability, the flocs tend to become less stable and lose strength over time. The majority of natural biopolymers comprise hydrolysable groups alongside the main chain making them susceptible to biodegradation via hydrolysis. Furthermore, several anionic bio-flocculants such as alginate, cellulose, and tannin are efficient only to a certain extent and can only assist the coagulation process. Cationic coagulant is necessary for the neutralisation of charge before bio-flocculant can bridge the microflocs together in the coagulation-flocculation process, and a high dose is required for efficient flocculation. To solve all of these difficulties, a new generation of smart biopolymer flocculants has been produced by optimally grafting synthetic polymeric branches onto pure polysaccharide backbones [18]. Research focusing on the development and characterisation of nano-bio-flocculants with a longer shelf life is being carried out recently. The areas of improvement include selection and identification of new raw materials, the simplification and improvement of extraction methods, improving functional properties and identifying new modifying agents, and industrial-scale-up of this technology.

8 Summary and Conclusion

Natural (bio-)polymers, particularly cellulose, chitosan, and proteins-based polymers, offer remarkable adsorption capacities for wastewater treatment, as well as are cheap, sustainable, and eco-friendly [43]. These properties make biopolymer-based materials a preferred alternative to currently available commercial adsorbing materials. However, large industrial-scale application of biopolymers for removal of organic dyes and heavy metals from fresh water and wastewater is still limited due to high cost, and incapability to remove multiple contaminants simultaneously. In addition, other factors such as the recovery of biopolymers, and the separation of pollutants like heavy metals from the adsorbing material after the adsorption process are critical to outcompete with prevailing adsorbents for commercial wastewater treatment [26].

Irrespective of the disadvantages, biopolymer-based products have a bright future in industrial wastewater remediation. In comparison to their competitors for wastewater purification, biopolymer-based materials offer greater removal efficiency with low input cost, and thus are predicted to see a rise in demand [1]. The development of novel biopolymers with high performance and low environmental impact opens new avenues for researchers and provides them with a variety of chances to better understand and address water pollution challenges. In the coming years, improvements in biopolymer-based products at the commercial scale will provide sustainable and renewable materials for wastewater remediation [32]. Existing technologies are currently incapable of extracting all microbial polysaccharides. The greatest impediment to the marketing of novel polysaccharides is the identification of new or better qualities than those found in existing products. The second impediment to improving original structures is the expense of production and development, which could be a limiting factor once again [14].

Due to their low cost and environmental friendliness, many biopolymers are now utilised in different industries and will be used more in the future. Blending and grafting are two strategies that have been developed to improve the characteristics of biopolymers [43]. Biopolymers are used to make a variety of composites and nanocomposites. Biopolymers' applications include the areas such as bio-medical, tissue engineering, food and packaging industry and automotive industry [20]. Therefore, biopolymers will play an important role in the daily needs of human life in the future.

References

1. Ajao V et al (2021) Bioflocculants from wastewater: Insights into adsorption affinity, flocculation mechanisms and mixed particle flocculation based on biopolymer size-fractionation. J Colloid Interface Sci 581:533–544. https://doi.org/10.1016/j.jcis.2020.07.146
2. Asif MB et al (2021) '21—Polysaccharide-derived biopolymeric nanomaterials for wastewater treatment. In Kanwar S et al (eds) Biopolymeric nanomaterials. Elsevier (Micro and Nano Technologies), pp 447–469. https://doi.org/10.1016/B978-0-12-824364-0.00012-5

3. Chang YC, Chang SW, Chen DH (2006) Magnetic chitosan nanoparticles: studies on chitosan binding and adsorption of Co (II) ions. React Funct Polym 66(3):335–341
4. Chaudhary S, Sharma J, Kaith BS, Yadav S, Sharma AK, Goel A (2018) Gum xanthan-psyllium-cl-poly (acrylic acid-co-itaconic acid) based adsorbent for effective removal of cationic and anionic dyes: adsorption isotherms, kinetics and thermodynamic studies. Ecotoxic Environ Safety 149:150–158
5. Chen B et al (2020) Magnetic chitosan biopolymer as a versatile adsorbent for simultaneous and synergistic removal of different sorts of dyestuffs from simulated wastewater. Chem Eng J 385:123926. https://doi.org/10.1016/j.cej.2019.123926
6. Fertah M et al (2017) Extraction and characterization of sodium alginate from Moroccan Laminaria digitata brown seaweed. Arab J Chem 10:S3707–S3714. https://doi.org/10.1016/j.arabjc.2014.05.003
7. Fouda-Mbanga BG, Prabakaran E, Pillay K (2021) Carbohydrate biopolymers, lignin based adsorbents for removal of heavy metals (Cd2+, Pb2+, Zn2+) from wastewater, regeneration and reuse for spent adsorbents including latent fingerprint detection: a review. Biotechnol Reports 30:e00609. https://doi.org/10.1016/j.btre.2021.e00609
8. Golie WM, Upadhyayula S (2017) An investigation on biosorption of nitrate from water by chito- san based organic-inorganic hybrid biocomposites. Int J Biol Macromol 97:489–502
9. Habiba U, Afifi AM, Salleh A, Ang BC (2017) Chitosan/(polyvinyl alcohol)/zeolite electrospun composite nanofibrous membrane for adsorption of Cr6C, Fe3C and Ni2C. J Hazard Mater 322:182–194
10. Huang CH, Hsieh TH, Chiu WY (2015) Evaluation of thermally crosslinkable chitosan-based nanofibrous mats for the removal of metal ions. Carbohydr Polym 116:249–254
11. Jacob J, Gopi S (2021) Isolation and physicochemical characterization of biopolymers. Biopol Indus Appl.https://doi.org/10.1016/b978-0-12-819240-5.00003-1
12. Joly N et al (2020) Interaction of metal ions with mono-and polysaccharides for wastewater natural products chemistry & research interaction of metal ions with mono- and polysaccharides for wastewater treatment : a review. Nat Products Chem Res 8:1–17. https://doi.org/10.35248/2329-6836.20.8.373
13. Kartik A et al (2021) A critical review on production of biopolymers from algae biomass and their applications. Bioresource Technol 329:124868. https://doi.org/10.1016/j.biortech.2021.124868
14. Kawalkar A (2014) A comprehensive review on biopolymers. Scientific Rev Chemi Commun 4(2):61–68
15. Khurana P et al (2020)'HAHmiR.DB: a server platform for high-altitude human miRNA-gene coregulatory networks and associated regulatory circuits. Database. https://doi.org/10.1093/DATABASE/BAAA101
16. Łabowska MB, Michalak I, Detyna J (2019) Methods of extraction, physicochemical properties of alginates and their applications in biomedical field—a review. Open Chem 17(1):738–762. https://doi.org/10.1515/chem-2019-0077
17. Lazaridis NK, Keenan H (2010) Chitosan beads as barriers to the transport of azo dye in soil col- umn. J Hazard Mater 173:144–150
18. Lee CSCS, Robinson J, Chong MFMF (2014) A review on application of flocculants in wastewater treatment. Process Saf Environ Prot 92(6):489–508. https://doi.org/10.1016/j.psep.2014.04.010
19. Li Y, Qiu TB, Xu XY (2013a) Preparation of lead-ion imprinted crosslinked electrospun chitosan nanofiber mats and application in lead ions removal from aqueous solutions. Eur Polym J 49:1487–1494
20. Lutzu GA et al (2021) Latest developments in wastewater treatment and biopolymer production by microalgae. J Environ Chem Eng 9(1):104926. https://doi.org/10.1016/j.jece.2020.104926
21. Maji B, Maiti S (2021) Chemical modification of xanthan gum through graft copolymerization: tailored properties and potential applications in drug delivery and wastewater treatment. Carbohydrate Poly 251:117095. https://doi.org/10.1016/j.carbpol.2020.117095

22. Martins PSDO, De Almeida NF, Leite SGF (2008) Application of a bacterial extracellular polymeric substance in heavy metal adsorption in a co-contaminated aqueous system. Braz J Microbiol 39(4):780–786. https://doi.org/10.1590/S1517-83822008000400034
23. Maćczak P, Kaczmarek H, Ziegler-Borowska M (2020) Recent achievements in polymer bio-based flocculants for water treatment. Materials 13(18):https://doi.org/10.3390/ma13183951
24. McDowall DJ, Gupta BS, Stannett VT (1984) Grafting of vinyl monomers to cellulose by ceric ion initiation. Prog Polym Sci 10(1):1–50
25. Min LL, Yuan ZH, Zhong LB, Liu Q, Wu RX, Zheng YM (2015) Preparation of chitosan based electrospun nanofiber membrane and its adsorptive removal of arsenate from aqueous solution. Chem Eng J 267:132–141
26. Mtibe A et al (2021) Synthetic biopolymers and their composites: advantages and limitations-an overview. Macromol Rapid Commun 42(15):e2100130. https://doi.org/10.1002/marc.202100130
27. Nasrollahzadeh M et al (2021) Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano)materials for sustainable water treatment: a review. Carbohydrate Poly 251:116986.https://doi.org/10.1016/j.carbpol.2020.116986
28. No HK, Meyers SP (2000) Application of chitosan for treatment of wastewaters. Revi Environ Contamination Toxicol 163:1–27. https://doi.org/10.1007/978-1-4757-6429-1_1.
29. Olivera S et al (2016) Potential applications of cellulose and chitosan nanoparticles/composites in wastewater treatment: a review. Carbohyd Polym 153:600–618. https://doi.org/10.1016/j.carbpol.2016.08.017
30. Pal A, Majumder K, Bandyopadhyay A (2016) Surfactant mediated synthesis of poly(acrylic acid) grafted xanthan gum and its efficient role in adsorption of soluble inorganic mercury from water. Carbohyd Polym 152:41–50. https://doi.org/10.1016/j.carbpol.2016.06.064
31. Pal P et al (2021) Applications of chitosan in environmental remediation: a review. Chemosphere, 266. https://doi.org/10.1016/j.chemosphere.2020.128934
32. Pandey J (2020) Biopolymers and their application in wastewater treatment. https://doi.org/10.1007/978-981-15-1390-9_11
33. Qi X et al (2021) Recent advances in polysaccharide-based adsorbents for wastewater treatment. J Cleaner Prod 315:128221. https://doi.org/10.1016/j.jclepro.2021.128221
34. Rawat P et al (2018) Phytochemical analysis and evaluation of in vitro immunomodulatory activity of Rhododendron Arboreum leaves. Asian J Pharm Clin Res 11(8):123–128. https://doi.org/10.22159/ajpcr.2018.v11i8.25372
35. Rebah FB, Mnif W, Siddeeg SM (2018) Microbial flocculants as an alternative to synthetic polymers for wastewater treatment: a review. Symmetry 10(11):1–19. https://doi.org/10.3390/sym10110556
36. Rezaee A, Ramavandi B, Ganati F, Ansari M, Solimanian A (2006) Biosorption of mercury by biomass of filamentous algae Spirogyra species. J Biol Sci 6:695–700
37. Russo T et al (2021) Sustainable removal of contaminants by biopolymers: a novel approach for wastewater treatment. current state and future perspectives. Processes 9(4). https://doi.org/10.3390/pr9040719
38. Salehi E, Daraei P, Arabi Shamsabadi A (2016) A review on chitosan-based adsorptive membranes. Carbohydr Polym 152:419–432
39. Saravanan R, Ravikumar L (2015) The use of new chemically modified cellulose for heavy metal ion adsorption and antimicrobial activities. J Water Resour Prot 7:530–545
40. Sarode S et al (no date) Title: overview of wastewater treatment methods with special focus on biopolymer chitin- chitosan Abstract Heavy metals have substantively high values of half-lives with nonbiodegradable chemical nature . At the same time, their ionic compounds have ama
41. Schmidt B, Kowalczyk K, Zielinska B (2021) Synthesis and characterization of novel hybrid flocculants based on potato starch copolymers with hollow carbon spheres. Materials 14(6). https://doi.org/10.3390/ma14061498
42. Shaikh MAJ et al (2021) Current update on psyllium and alginate incorporate for interpenetrating polymer network (IPN) and their biomedical applications. Int J Biol Macromol 191:432–444. https://doi.org/10.1016/j.ijbiomac.2021.09.115

43. Udayakumar GP et al (2021) Ecofriendly biopolymers and composites: Preparation and their applications in water-treatment. Biotechnol Adv 52:107815. https://doi.org/10.1016/j.biotechadv.2021.107815
44. Wang T, Jin X, Chen Z, Megharaj M, Naidu R (2014) Green synthesis of Fe nanoparticles using eucalyptus leaf extracts for treatment of eutrophic wastewater. Sci Total Environ 466:210–213
45. Wang S et al. (2021) Advances in microbial remediation for heavy metal treatment: a mini review. J Leather Sci Eng. https://doi.org/10.1186/s42825-020-00042-z
46. Xia S et al (2020) Application of polysaccharide biopolymer in petroleum recovery. Polymers 12(9). https://doi.org/10.3390/polym12091860
47. Yue Y et al (2019) A novel polyamidine-grafted carboxymethylcellulose: synthesis, characterization and flocculation performance test. E-Polymers 19(1):225–234. https://doi.org/10.1515/epoly-2019-0023
48. Zhang C et al (2017) Phenylalanine ammonia-lyase2.1 contributes to the soybean response towards Phytophthora sojae infection. Sci Rep 7(1):1–13. https://doi.org/10.1038/s41598-017-07832-2
49. Zhao N et al (2020) Synthesis of polymer grafted starches and their flocculation properties in clay suspension. Minerals 10(12):1–12. https://doi.org/10.3390/min10121054
50. Zhao C et al (2021) Application of coagulation/flocculation in oily wastewater treatment: a review. Sci Total Environ 765:142795. https://doi.org/10.1016/j.scitotenv.2020.142795
51. Zubair M, Ullah A (2021) Chapter 14—Biopolymers in environmental applications: industrial wastewater treatment. In Thomas S, Gopi S, Amalraj A (eds) biopolymers and their industrial applications. Elsevier, pp 331–349. doi: https://doi.org/10.1016/B978-0-12-819240-5.00014-6