Chapter 11
Biopolymers and Their Application in Wastewater Treatment

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Abstract Due to heavy industrialization and urbanization, the conservation of the environment has become increasingly important in view of the raised ecological problems. The discharge of huge quantities of effluents from industries and municipalities into rivers and lakes makes the condition vulnerable for sustainable life. The presence of organic toxics such as dyes and heavy metals, such as chromium, mercury, cadmium, cobalt, copper, nickel, lead, zinc and tin, in our water resources may cause serious health hazards to living organisms. Various technologies for removal of toxic chemicals and ions from industrial and agricultural effluents have been introduced such as adsorption, coagulation, flocculation, precipitation, co-precipitation, solvent extraction, ion exchange and membrane technology. However, most of these techniques require synthetic toxic reagents which are expensive too and hence the capital cost for treatment increases. The wide availability, biodegradability, non-toxicity and relatively inexpensiveness of biopolymers present an attractive alternative to such toxic synthetic and chemical products. In this context, several biopolymers were chemically refined to work as cationic or anionic agents for wastewater treatment. The book chapter summarizes the research carried out on the use of biopolymers to remove heavy metal and toxic chemicals from solutions and effluents. The various biopolymers (e.g. cellulose, chitosan, tannin, alginate, gums and mucilage), their classification, mechanisms of action, factors and their application in wastewater treatment in the scientific literature are analysed and compiled.

Keywords Industries · Wastewater · Biopolymers · Application · Treatment

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11.1 Introduction

Water is the most important and essential element on the mother earth for sustainable life. Alarming growth in population, urbanization, industrialization, agricultural activities, climate change and socio-economic growths, along with high living standards, have generated ever-lasting demands for water resources (Kishor et al. 2019; Zainith et al. 2019). However, due to this heavy population load and human activities, quality of our water resources is deteriorating continuously (Bharagava et al. 2008; Chandra et al. 2009). Every year, millions of tons of different types of wastes such as industrial sewage water containing thousands of organic (fertilizers, pesticides, detergents, plasticizers, pharmaceuticals, hydrocarbons, biphenyls, phenols, oils, greases), inorganic (heavy metals, compound containing, fluoride, phosphate, sulfate, nitrate) and biological pollutants or contaminants (virus, bacteria, fungi, algae, amoebas and planktons) have been released into our water resources (Bharagava et al. 2018; Saxena et al. 2019). Such kind of introduction of pollutants or contaminants from industrial, agricultural and natural disposals to our water resources is a major environmental and health concern (Bharagava and Chandra 2010; Kishor et al. 2019). In this regard, water treatment plays a significant role in improving public health and environmental quality.

Several methods have been developed and applied for water and wastewater treatment including precipitation, co-precipitation, solvent extraction, adsorption, coagulation, flocculation, ion exchange and membrane technology (Patterson 1989; Brooks 1991; Chmielewski et al. 1997; Blais et al. 1999). These methods are exploited to reduce pollutants or contaminants from industrial wastewater and to remove toxic chemicals from sewage including municipal sanitary sewers and to recover the quality of raw drinking water. Most of these methods have utilized inorganic compounds, e.g. alum and $FeCl_3$, or organic polymers, e.g. polyacrylamides, which have their own benefits and drawbacks when their applicability and pollutant remediation efficacy is considered (Ahmad et al. 2008; Ashraf et al. 2013a).

In recent years, biopolymers illustrate an attractive alternative to synthetic inorganic and organic compounds because of following properties (Bolto and Gregory 2007):

1. Abundance and cheap resource make biopolymers economically viable.
2. The presence of large number of active functional groups such as amino and hydroxyl groups which increases adsorption capacity of biopolymers for many pollutants or contaminants.
3. Tendency to get modified through physical or chemical methods for more versatile applications.
4. They are safe, biodegradable, non-toxic and environment-friendly in nature.

In addition to above properties, the sludge obtained after wastewater treatment by biopolymers can be efficiently degraded by microorganisms due to its biodegradable nature (Renault et al., 2009a). Adsorption, coagulation and flocculation are the main methods applied by the biopolymers for water and wastewater treatment. The adsorption capacity of biopolymers is an important parameter for disposing of many kinds of pollutants from waste or polluted water. The availability of a wide range of biopolymer-based adsorbents and their ease of operation makes this method most popular among all the methods available for wastewater treatment.

In coagulation or flocculation methods biopolymers can destabilize the large colloidal particles by increasing the ionic strength and decreasing the zeta potential so that there is a significant decrease in the thickness of the diffuse part of the electrical double layer that takes place. In another way, biopolymers with macromolecular structures and a variety of functional groups (e.g. carboxyl and hydroxyl groups) can interact with contaminants by adsorbing counter ions and neutralize the particle charge (Özacar and Şengil 2003). For many years, several biopolymers such as tannins, cellulose, alginate, chitosan, gums and mucilage have been attracting wide interest of researchers for developing advanced adsorbents and flocculants for wastewater treatment. In this context, herein we summarize all the aspects of biopolymers along with their role in water treatment.

11.2 Biopolymers and Their Classification

Biopolymer is a new generation polymeric material. These polymers are made up of covalently bonded monomeric units which form chain-like arrangement of molecules. The prefix ‘bio’ denotes its natural origin and biodegradable nature of biopolymers. Biopolymers are environment-friendly molecules which can be degraded by naturally occurring organisms; only organic by-products such as carbon dioxide and water are generated which have no harmful effect on the environment. The versatile nature of biopolymers such as biodegradability, renewability and abundance makes biopolymers an attractive alternative material to petroleum-derived plastics. The broad classification of biopolymers is shown in Fig. 11.1 (Vieira et al. 2011).

Several biopolymers are of both bio-based and fuel-based origin such as PTT, PBS and PLA, although PLA is mainly produced by fermentation from renewable resources such as sugar cane and starch and can also be synthesized from fossil fuels.

11.3 Mechanism of Action of Biopolymers for Wastewater Treatment

11.3.1 By Bridge Formation

Polymer bridge formation takes place when long chain polymers with high molecular weight and low charge density are adsorbed onto the surface of more than one particle in such a way that long loops and tails extend or stretch some way into solution and thus these ‘hanging’ polymeric segments create ‘bridging’ between particles (Fig. 11.2) (Lee et al. 2012; Caskey and Primus 1986; Biggs et al. 2000;

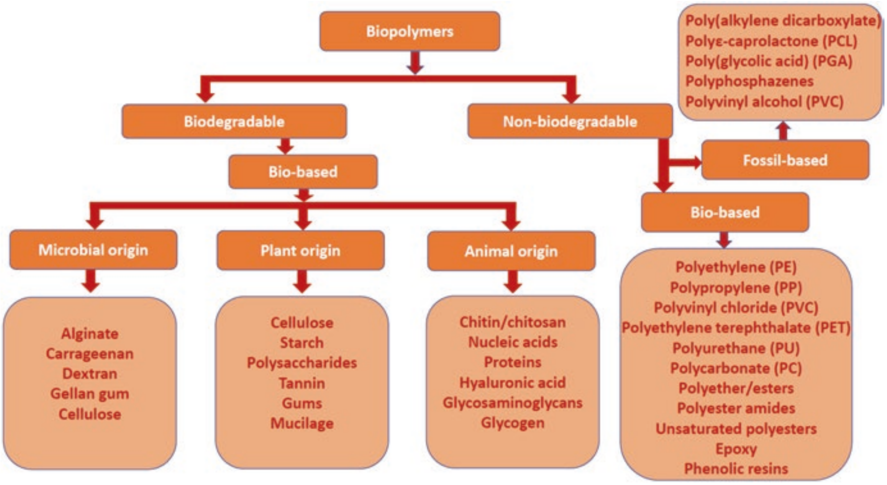


Fig. 11.1 Broad classification of biopolymer

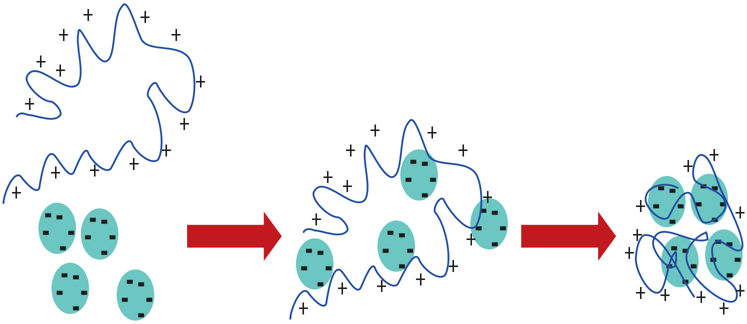


Fig. 11.2 Mechanism of bridge formation

Blanco et al. 2002). The long polymeric chains which can extend from one particle surface to another are required for effective bridging (Razali et al. 2011). In addition, there should be enough unoccupied surface on a particle for attachment of polymeric chains adsorbed on other particles. In general, for bridge formation an excessive amount of polymer is required; otherwise the particle surfaces will be exaggeratedly coated with polymer and no vacant sites will be available to ‘bridge’ with other particles (Fig. 11.2) (Sher et al., 2013). However, the adsorbed amount should not be too low because it will cause lesser number of bridge formation. In this way, it has been well established that polymer bridging provides much larger and stronger flocks than those formed in other ways.

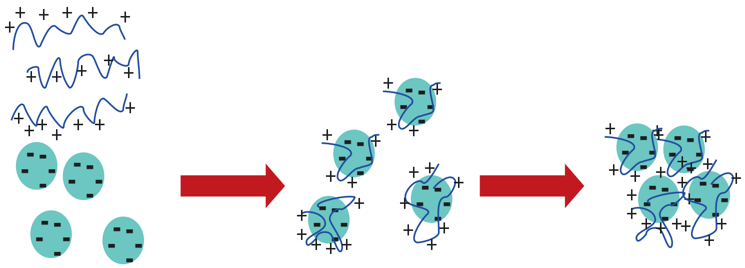


Fig. 11.3 Mechanism for electrostatic patch

11.3.2 By Electrostatic Patch

When bridging capability of long chain polymer is reduced, another possibility arises, which is known as ‘electrostatic patch’ mechanism (Fig. 11.3). The basic idea behind ‘electrostatic patch’ mechanism is that, when a highly charged cationic polymer adsorbs on a negatively charged surface, it is not physically possible for every negatively charged site on the surface to get neutralized by a cationic polymer chain (Blanco et al. 2002). This results into the formation of cationic ‘patches’ or ‘islands’ on negatively charged surfaces. The importance of ‘patchwise’ adsorption is that, as particles approach closely, strong electrostatic attraction between positive patches and negative zones occurred which can give rise to particle attachment (Bolto and Gregory 2007).

11.3.3 By Adsorption

Adsorption is a surface phenomenon where one or more adsorbates are attracted towards the adsorbent with which they are in interaction and bonded to its surface through liquid-solid intermolecular forces of attraction and get deposited at the solid surface (Fig. 11.4). It follows common mechanism for inorganic and organic pollutant removal. The adsorption phenomenon can be categorized as: (1) physisorption (involving weak van der Waals forces), (2) chemisorption (involving covalent bonding) or electrostatic sorption (involving ionic bonding) (Ashraf et al. 2013b).

As the adsorption proceeds, an equilibrium is established for adsorption of the solute between the solution and adsorbent. At equilibrium, the adsorption amount of adsorbate (q_e, mmol g^{-1}) can be calculated according to the following Eq. (11.1):

$$q_e = V\left(C_0 - C_e\right) / M \tag{11.1}$$

where V is the volume of solution (L), M is mass of monolithic adsorbents (g), C_0 is the initial adsorbate concentrations and C_e is the equilibrium adsorbate concentrations.

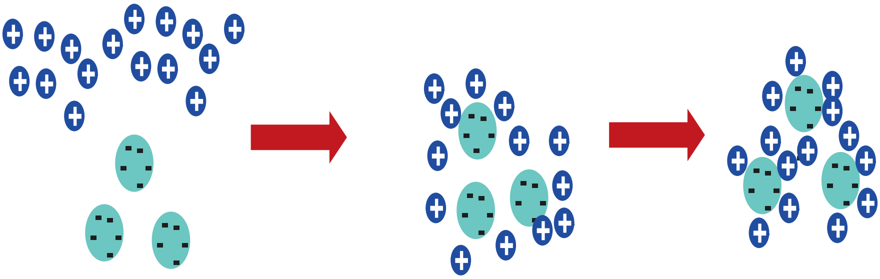


Fig. 11.4 Mechanism of adsorption

11.3.4 By Coagulation/Flocculation

Coagulation/flocculation is one of the most widely used solid-liquid separation processes which involve the removal of all kind of solids (suspended and dissolved) and colloidal and organic contaminants present in industrial wastewater (Renault et al. 2009b). Coagulation process involves charge neutralization which weakens colloidal matter and aggregates finely divided or dispersed particles into large masses (Fig. 11.5). These large masses adsorb dissolved organic substances by an adsorption mechanism and can easily be eliminated by simple filtration and sedimentation (Sharma et al. 2006). These methods are simple and efficient for wastewater treatment and have found extensive application for the treatment of different types of wastewater (Yue et al. 2008; Ahmad et al. 2005; Tatsi et al. 2003; Wong et al. 2006; Zhong et al. 2003).

11.4 Effect of Factors on Efficacy of Biopolymers

11.4.1 Effect of pH

pH is identified as one of the most important parameters to judge the efficacy of biopolymers. The role of biopolymers in wastewater treatment is strongly dependent on pH, as it can affect the extent of positive or negative charge on the polymeric surface. For example, chitosan is a weak base and its dissociation equilibrium is represented by Eq. (11.2):

$$\text{Chitosan}-\text{NH}_3{}^{+}+\text{H}_2\text{O}\leftrightarrow\text{Chitosan}-\text{NH}_2+\text{H}_3\text{O}^{+} \tag{11.2}$$

Its dissociation equilibrium constant is given by Eq. (11.3):

$$K_\text{a}=\left[\text{Chitosan}-\text{NH}_2\right]\left[\text{H}_3\text{O}^{+}\right]/\left[\text{Chitosan}-\text{NH}_3{}^{+}\right] \tag{11.3}$$

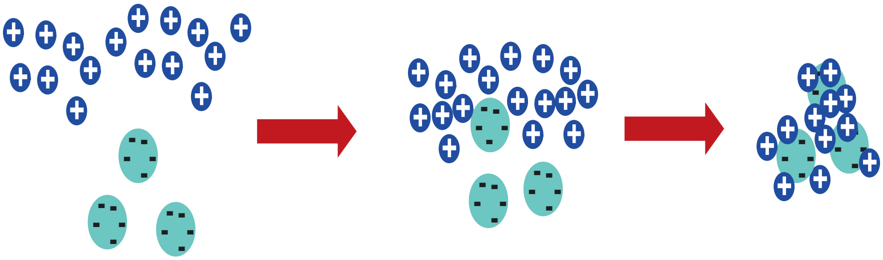


Fig. 11.5 Mechanism of coagulation

In acidic solutions, protonation of amine groups of chitosan is controlled by the p*K*a value and regulated by the charge density and extent of deacetylation (Guibal 2004). In general, p*K*a values fluctuate between 6.3 and 7.2 which directly depend on the extent of deacetylation (Sorlier et al. 2001) and are helpful in understanding the electrostatic interactions of chitosan with cations and anions. Equation (11.2) clearly depicts the effect of pH on the generation of ammonium groups ($-NH_3^+$). At neutral pH, approximately 50% of the total amino group of chitosan is protonated (Guibal, 2004). At particular pH when the protonation of amino groups is high, the tendency to adsorb metal anions is also increased (Ashraf et al., 2012). The overall number of protonated amino groups declines by increasing the pH level, and then the tendency towards metallic cations increases.

11.4.2 Effect of Size

The efficiency of biopolymers mainly depends on their physico-chemical characteristics such as porosity, surface area and particle size of biopolymer. In general, biopolymers in their native form are non-porous and possess low surface area; e.g. chitosan has a very low specific area ranging between 2 and 30 $m^2\ g^{-1}$. Modification of biopolymer either by crosslinking or by grafting increases its adsorption performances (Chiou and Li 2002; Ruiz et al. 2000; Delval et al. 2003). In general, adsorption capacity varies in irregular manner on variation in the particle size (Delval et al. 2003). The adsorption or flocculation increases with decrease in size of the particle as the effective surface area is quite high for the same mass of smaller particles, and hence the time required to achieve the equilibrium significantly increases with the size of biopolymer. The influence of this parameter also depends on several other factors such as the chemistry of the pollutant, the physiochemical characteristics of the biopolymer such as its crystallinity, the degree of crosslinking and the rigidity of the polymeric chains (Ruiz et al. 2000).

11.4.3 Effect of Dose of Biopolymers

In general, the removal efficiency of biopolymers improved by increasing its dosage. This is due to the fact that the higher dose of biopolymers in the solution provides greater availability of exchangeable sites for the metal ions and pollutants. However, after a certain dose of biopolymer, the maximum adsorption is achieved and an equilibrium is established between bounded and unbounded free ions in the solution. On attainment of equilibrium, the concentration of free ions remains constant even with further addition of the dose of biopolymer (Ramya et al. 2011).

11.4.4 Effect of Contact Time

Generally, at the beginning of the treatment, the removal rate of metal ions increases with increase in contact time. Afterwards removal rate slowed down and equilibrium is achieved. Therefore, equilibrium time is among the important parameters responsible for an economical wastewater treatment system (Ramya et al. 2011).

11.4.5 Effect of Temperature

The adsorption capacities of biopolymer increase with increasing temperature. This phenomenon is quite common among biopolymer-based adsorbent and is due to the fact that increasing temperature not only increases the mobility of the ions, but may also produce a swelling effect within the internal structure of the biopolymer. However, after optimum temperature the number of adsorbed ions on adsorbent decreases due to the predominance of desorption step (Wong et al. 2008).

11.5 Biopolymers for Wastewater Treatment

The wastewater produced from various types of industries contains large amount of fine suspended and dissolved solids, organic and inorganic matter, metals and toxic chemicals. Various traditional and advanced technologies have been utilized to remove such impurities from wastewater, such as precipitation, ion exchange, solvent extraction, membrane filtration, adsorption, coagulation, flocculation and electrolytic and biological methods (Radoiu et al. 2004). Among these methods, adsorption, coagulation and flocculation are the most widely used separation process for the removal of heavy toxic metals and chemicals, suspended and dissolved solids and colloids present in industrial wastewater (Renault et al. 2009b). These are simple and efficient methods for wastewater treatment and have found extensive application in wastewater treatment.

Over the past few decades, several research studies have been pursued to develop cost-effective and easily available biopolymer-based adsorbent, flocculant and coagulant for wastewater treatment. Chitosan, cellulose, alginates, tannins, gum and mucilage are some well-known biopolymers that have attracted wide interest of researchers for the development of efficient materials for water treatment. In this section, we will discuss these biopolymers and their derivatives that have been developed to increase their efficacy in removal of toxic chemicals and heavy metals from wastewater.

11.5.1 Chitosan

Chitosan is a linear amino-polysaccharide containing *N*-glucosamine and *N*-acetyl-D-glucosamine monomeric units (Fig. 11.6). The arrangement and distribution of these two monomeric units along the chain determine the physical, chemical and biological properties of the biopolymer (Anitha et al. 2014).

Chitosan is obtained from the alkaline deacetylation of chitin, a biopolymer extracted from crustaceans, arthropods, fungi, bacteria and other organisms (Rinaudo 2006; Yen and Mau 2007) as shown in Fig. 11.7.

Deacetylation exposes the amine groups responsible for its cationic behaviour and necessarily required for adsorption (Jaafari et al. 2004). Chitosan has found extensive application in various fields due to its cationic behaviour and serving as most promising biopolymer for the development of new materials. The availability of free amine groups determines the solubility of chitosan; in general, chitosan is insoluble in water and organic solvents but soluble in dilute weak organic acids such as acetic acid and formic acid (Renault et al. 2009a; Szyguła et al. 2009). At acidic pH the free amino groups of chitosan are completely protonated and provide high charge density (Rinaudo 2006; Guibal and Roussy 2007) to the cationic biopolymer. Thus, acidic solution of chitosan produces protonated amine groups along the chain and facilitates electrostatic interactions with anionic contaminants such as dyes, heavy metal anions, toxic organic compounds, etc. (Guibal et al. 2006; Renault et al. 2009a; No and Meyers 2000), and makes it effective for wastewater treatment.

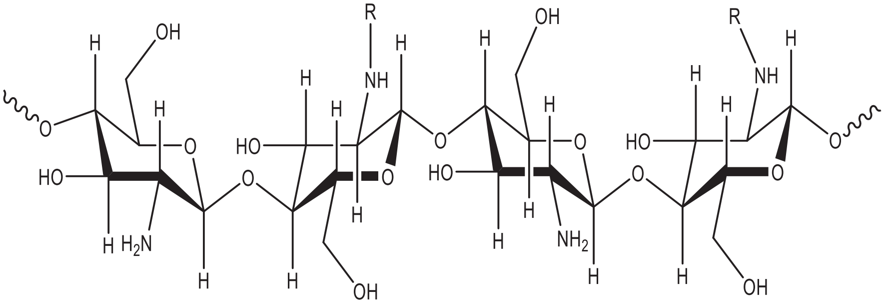


Fig. 11.6 Structure of chitosan, where R=Ac or H depending on the degree of acetylation

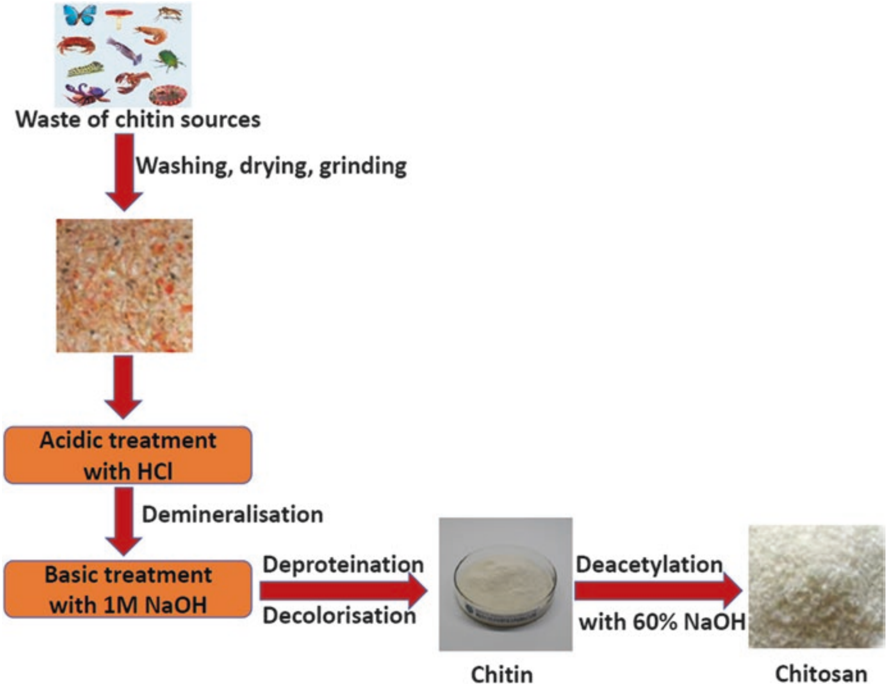


Fig. 11.7 Extraction of chitosan

Chitosan is a non-toxic, biodegradable, biocompatible and nonimmunogenic natural polymer with the existence of modifiable positions in chemical structure and hence has potential to be processed in many forms (Anitha et al. 2014). The chitosan molecule can be modified either by physical modifications or by chemical modifications to beads, films, hydrogels, nanofibers, nanocomposites and nanopowder as shown in Fig. 11.8. Chemical modifications can be achieved either by grafting which involves insertion of functional groups or by crosslinking reactions; bonding the macromolecular chains with each other leads to the formation of chitosan derivatives with superior properties such as increase in adsorption capacity and resistance toward extreme medium conditions.

Different forms of chitosan like film (Salehi et al. 2016), nanofiber (Habiba et al., 2017), powder (Chang et al. 2006) and beads (Lazaridis and Keenan 2010) were obtained through various physical modifications. Recently, chitosan-based composites have been reported which not only overcome the drawbacks of chitosan but also offer physical strength and magnetism (Golie and Upadhyayula 2017; Liu et al. 2015).

In recent years, scientists have focused their attention on development of chitosan nanofibers with customizable pore sizes and rationally high specific surface areas (Li et al. 2013a; Huang et al. 2015). Min et al. 2015 synthesized pure chitosan electrospun nanofiber membranes (average diameter ~ 129 nm) to remove As (V) from water. Habiba et al. (2017) have used blending and electrospinning methods for the production of chitosan/(polyvinyl alcohol)/zeolite composite nanofibers.

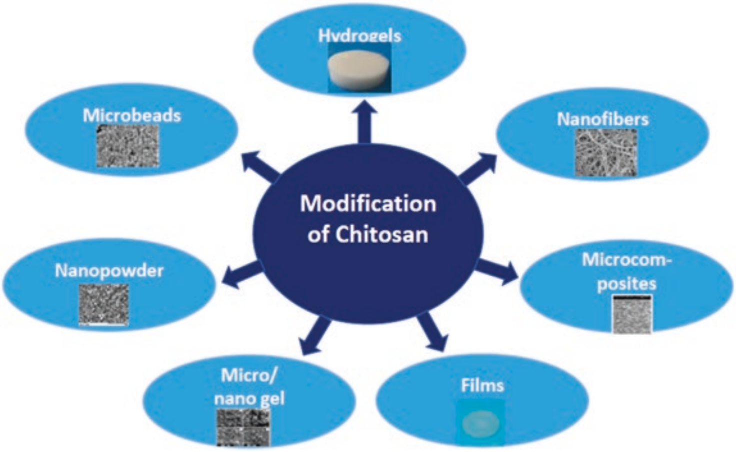


Fig. 11.8 Different forms of chitosan used in wastewater treatment

These composite nanofibers have shown good stability in solutions at different pH and with recycling up to five runs. Various chitosan derivatives with good adsorption capacity together with good mechanical resistance and chemical stability could be synthesized via chemical modification.

Chemical modification can be achieved through different kinds of reactions such as esterification, xanthation, oxidation (Zhu et al. 2012; Chen and Wang 2012), acylation (Repo et al. 2013; Guo et al. 2016), etherification (Viswanathan et al. 2009; Ge and Luo 2005), Schiff base reaction (Tanhaei et al. 2015; Elwakeel et al. 2017), phosphonium enhancement (Sessarego et al. 2019) and alkylation (Qin et al. 2003; Cárdenas et al. 2001). Numerous studies have clearly demonstrated the outstanding coagulation and flocculation properties of chitosan for dye molecules in textile wastewater (Szyguła et al. 2009), heavy metals and phenolic molecules in cardboard-mill wastewater (Renault et al. 2009b) organic matter in pulp and paper mill wastewater (Rodrigues et al. 2008) and inorganic suspensions in kaolinite suspension (Li et al. 2013b). This wide range of application clearly demonstrates the potential of chitosan and chitosan derivatives for water and wastewater treatment.

11.5.2 Cellulose

Cellulose is a long linear chain polymer of β-D-glucopyranose repeat units linked together by β-1,4-glycosidic linkage (Fig. 11.9). It is one of the most abundant natural polysaccharides among all the polymers present on earth and derived from different wood sources as shown in Fig. 11.10. The characteristic property of chirality, hydrophilicity or hydrophobicity and degradability of cellulose largely depends on its molecular structure. As pure cellulose has very limited applications, in recent years, serious efforts have been taken to modify its properties by improving its physical and chemical structure which broaden its industrial applications (Das et al. 2012).

Fig. 11.9 Cellulose-β-1,4-linkage

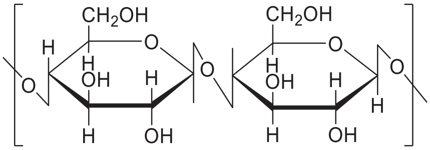
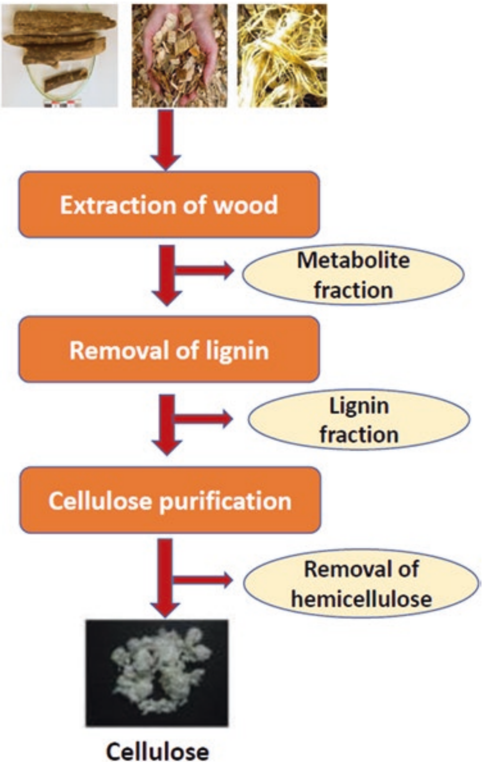


Fig. 11.10 Extraction of cellulose from wood sources



There are two main approaches for the conversion of cellulose into its derivatives. The first approach involves a direct introduction of chelating or metal binding functionalities into the cellulose backbone (Saravanan and Ravikumar 2015) whereas alternative approach involves grafting of selected monomers to the cellulose backbone (Aoki et al. 1999; Singh and Guleria 2014; Kumar et al. 2019b). Such kind of chemical modifications not only increases the adsorption capacity of cellulose derivatives for heavy metals in aqueous and nonaqueous media (Kamel et al. 2006) but also used to vary several other properties of cellulose, such as absorptivity, hydrophobicity or hydrophilicity, elasticity and microbial, heat and mechanical resistance (McDowall et al. 1984). The most important functionalization processes of cellulose occur through etherification, esterification, oxidation and halogenation (O'Connell et al. 2008).

In another study, Khiari et al. (2010) prepared anionic sodium carboxymethylcellulose from agricultural waste, i.e. date palm rachis coupled with aluminium sulphate as coagulant, and tested it as eco-friendly flocculants for removal of turbidity in drinking water treatment. Recently, Suopajärvi et al. (2013) have reported anionized nanocellulose flocculant with ferric sulphate coagulant and examined its flocculating properties in municipal wastewater.

11.5.3 Alginates

In 1881, alginate was first isolated by Stanford (1881). Alginate is present as sodium, magnesium and calcium salts of alginic acid in different species of brown seaweed (Phaeophyceae). Therefore, commercial alginates are extracted from *M. pyrifera*, *S. japonica*, *A. nodosum* and *L. hyperborea* (Gomez et al. 2009). In addition to seaweed origins, bacterial origin alginates are also reported; however, such kind of alginate is not yet commercially available (Mærk 2014). The process of extraction of alginate has been well documented in the literature and is relatively straightforward as shown in Fig. 11.11 (Smith and Miri 2010).

Alginate is a heteropolysaccharide of two uronic acid monomers, i.e. 1→4-linked β-ᴅ-mannuronic (MA) and 1→4-linked α-l-guluronic acid (GA) (Fig. 11.12). These residues are arranged randomly throughout the polysaccharide chain providing irregular geometry which impacts the packing ability of the polymeric chains. Such arrangements have significant impact on the physical properties of alginate. In general, large proportion of G blocks provides stiffer conformation and large proportion of M blocks provides more flexible conformation to corresponding alginates. The abundance of various functional groups such as hydroxyl, carboxylic and oxo groups gives alginic acid/salts strong chelating properties for metal ions.

Various chemical treatments such as phosphorylation, carboxylation and sulfonation may be applied on alginic acid in order to increase metal uptake capacity (Jeon et al. 2002); however, such treatments tend to increase the cost of the final product. A recent study investigated flocculating efficiency of sodium alginate in synthetic dye wastewater and in treatment of industrial textile wastewater by using aluminium sulphate as coagulant (Wu et al. 2012). Alginate derivatives were also studied for their capacity to adsorb different metals as shown in Table 11.1 and hence have a significant role in wastewater treatment.

11.5.4 Gum and Mucilage

Gums and mucilage have been emerged as a safer alternative to traditional polymers in wastewater treatment because their production and applications are environment-friendly and advantageous to human as well as for our ecosystem. Several natural adsorbents and flocculants based on gums and mucilage are derived from various

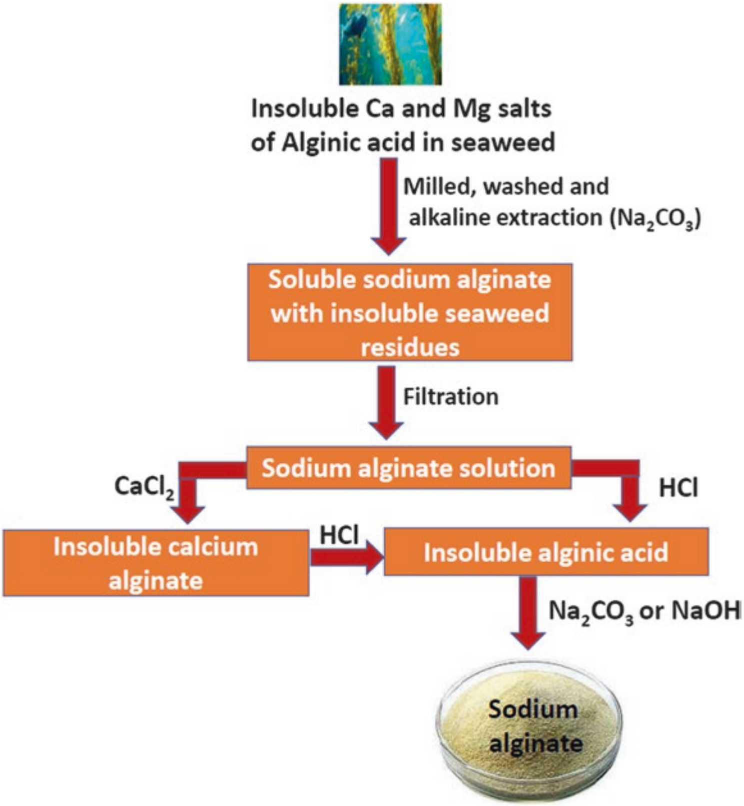


Fig. 11.11 Extraction of alginic acid from seaweed

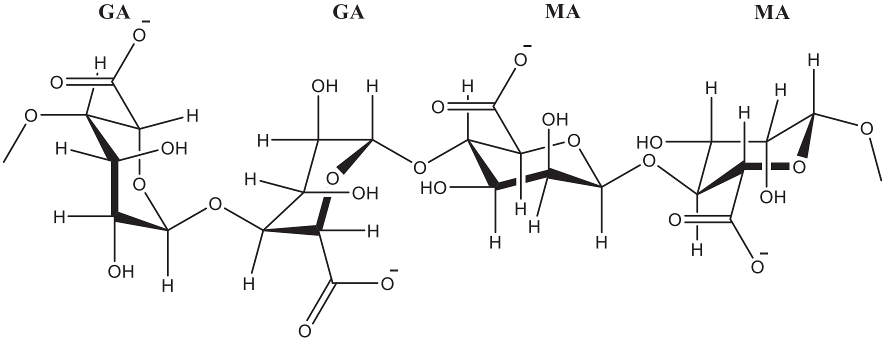


Fig. 11.12 Structure of alginate with repeat units of gluconic acid (GA) and mannuronic acid (MA)

Table 11.1 Metal sorption studies on alginate-based products

References	Adsorbent	Metals
Jeon et al. (2005)	Carboxylated alginic acid	Cu (II), Pb (II)
Karagunduz et al. (2006)	Dried alginate beads	Cu (II)
Al-Rub et al. (2004)	Alginate beads	Ni (II)
Papageorgiou et al. (2006)	Alginate beads	Cu (II), Cd (II), Pb (II)
Park and Chae (2004)	Alginate beads, alginate capsules, alginate gel coated	Pb (II)
Ablouh et al. (2019)	Chitosan microspheres/sodium alginate hybrid beads	Pb (II), Cr (VI)

plant species including *P. psyllium* (psyllium), *P. ovata* (isabgol), *T. foenum-graecum* (fenugreek), *H. esculentus* (okra), *T. indica* (tamarind) and *M. sylvestris* (mallow) and have shown promising results with regard to the treatment of textile wastewater (Mishra and Bajpai 2005), landfill leachate (Al-Hamadani et al. 2011), biological effluent (Anastasakis et al. 2009), sewage effluent (Mishra et al. 2003) and tannery effluent (Mishra et al. 2004).

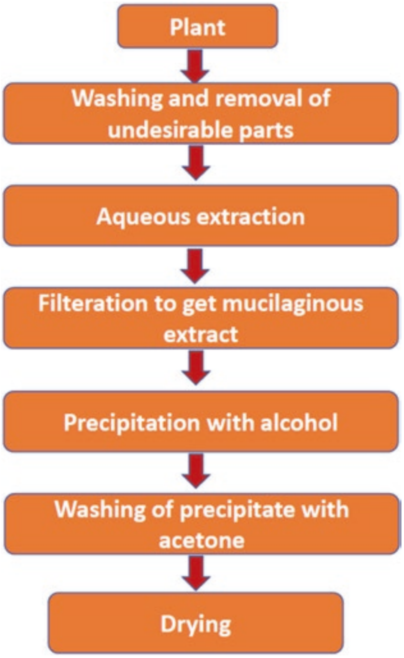
In some cases, their effectiveness was comparable to synthetic flocculants in terms of treatment efficiency even at low concentrations. Agarwal et al. (2001) and Mishra et al. (2004) have developed bio-flocculants from okra gum and fenugreek mucilage, respectively, and tested them for sewage wastewater and tannery effluent and found that the flocculation efficiency of these was at par with synthetic polyacrylamide. In general, these plant-based adsorbents/flocculants are obtained by aqueous extraction, filtration, precipitation with alcohol and drying as shown in Fig. 11.13.

Gum xanthan-psyllium-cl-poly(acrylic acid-co-itaconic acid)-based adsorbent has been synthesized and screened for effective removal of cationic and anionic dyes from the aqueous fluid. The adsorbent exhibited good removal and recyclability efficiency for the dyes auramine O (Aur-O) and eriochrome black T (EBT) with minimal activity decline after six and three cycles, respectively (Chaudhary et al. 2018). Most recently, binary grafted psyllium (Psy-g-Poly) was synthesized and tested for removal of Hg (II) ions from aqueous solution. The adsorbent exhibited high adsorption efficiency of about 96% at 100 ppm concentration of Hg (II) ions (Kumar et al. 2019a).

11.5.5 Tannin

Tannin is an anionic polymer (Özacar and Şengil 2000) obtained from vegetal secondary metabolites such as fruits, bark, leaves and others (Beltrán Heredia and Sánchez Martín 2009a, b) and biodegradable in nature. Its potential for wastewater treatment has been tested by removal of suspended pollutants from synthetic raw water (Özacar and Şengil 2000), removal of suspended and colloidal matter present in drinking water (Özacar and Şengil 2003) and removal of ink, pigments and dyes

Fig. 11.13 Processing steps for biopolymers from gum and mucilage



from ink-containing wastewater (Roussy et al. 2005). In all these studies, anionic tannin flocculated the destabilized colloidal particles by bridging and tucked them together to form flocs of large size which undergo sedimentation.

Modified tannin (Tanfloc) is obtained from the bark of *Acacia mearnsii* and further modified by a physico-chemical process is used to remove heavy metals from polluted surface water and in municipal wastewater treatment (Beltrán Heredia and Sánchez Martín 2009b). Chemical modification such as addition of hydrocolloid gums, soluble salts and generation of quaternary nitrogen to give Tanfloc cationic character makes it capable to directly use in wastewater treatment. New adsorbent poly(tannin-hexamethylendiamine) (PTHA) was developed by varying mole ratio of tannin and hexamethylendiamine under one-pot green synthesis method and used for Cr (VI) removal from aqueous solution (Liu et al. 2018). Most recently, tannin-supported on cellulose (TM) microfibers were successfully synthesized to remove cationic dye in aqueous solution (Wang et al. 2019).

11.6 Advantages and Current Challenges

With great awareness of potential harms caused by chemical and synthetic adsorbent and flocculants, most of the countries have started to strictly control its usage in drinking water and wastewater treatment. Researches are going on to replace the conventional flocculants by highly efficient and eco-friendly bio-adsorbent and flocculants. The biodegradability, non-toxicity, cost-effectiveness and easy availability from reproducible agricultural resources have attracted wide interest from researchers towards biopolymers for the development of new generation adsorbent and flocculants.

Several biopolymers such as alginates, starch, cellulose, chitosan, tannin, gums and mucilage have been investigated for their adsorbing and flocculating properties in wastewater treatment and they exhibit excellent selectivity towards toxic compounds and metals, thus efficient in the removal of pollutants from wastewater. However, it was reported that their applicability and feasibility is restricted by moderate absorbing and flocculating properties and short shelf life. This problem is addressed by developing modified biopolymers either by crosslinking or by grafting and such modified biopolymers are claimed to have remarkable pollutant removal properties and biodegradability.

There are several factors that constraint the development and application of modified biopolymers to pilot scale or in other industries such as chemicals used in the synthesis process of biopolymers may cause health and safety issues, complexity of synthesis process and requirement of high energy input for production of larger quantities and relatively high equipment cost for the synthesis restrict its application. In order to address all these challenges, exhaustive investigation is required to prove the validity of modified biopolymers and promote their industrial applications. More research is urgently required to derive maximum benefits of grafting and crosslinking technology and modified biopolymers in order to balance the high cost of scaling up and operation.

11.7 Conclusion

Due to the increasing demand of environment-friendly technologies for turbidity and contaminants, removal represents an important progress in sustainable environmental technology. Biopolymers are nontoxic, biodegradable and cheap and can be obtained from renewable resources and their application is directly related to the improvement of quality of life. Modification of biopolymers with chemical crosslinking and grafting has been studied recently to improve its characteristics. Several studies have been conducted to investigate the adsorbing or flocculating properties of biopolymers in wastewater treatment. The results verified that they are technically promising adsorbents and flocculants with high removal efficiency of toxic pollutants. All the studies of modified biopolymers took place under lab-scale conditions and their applications at industrial scale are still at their early stages. Therefore, for the sake of environment and human health, more qualitative and quantitative researches are required to be carried out to further exploit the potential of biopolymers in drinking and wastewater treatment plant.

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