

Chapter 2

Mechanistic Insight into the Coagulation Efficiency of Polysaccharide-based Coagulants

2.1 Polysaccharides-A Brief Overview

Polysaccharides possess the highest industrial capacity for adsorbents that can be useful as eco-friendly materials for water treatment, due to their prevalence [1–3]. Polysaccharides are stereoregular (natural) polymers of monosaccharides (sugars) also referred to as biopolymers. They are unique raw materials because they are inexpensive and widely available in many countries in the world. They possess biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, poly-functionality, high chemical reactivity, chirality, chelation and adsorption capacities. The excellent adsorption behaviour of polysaccharides is due to certain properties. These properties include (1) high hydrophilicity due to hydroxyl groups of glucose units; (2) presence of a vast number of functional groups (acetamido, primary amino, and/or hydroxyl groups); (3) high chemical reactivity of these groups; (4) flexible structure of the polymer chain [4]. The development of new products based on polysaccharides is a promising way to overcome the disadvantages of synthetic polymers and a better way of, rationally, using renewable bio-resources. Under environmental conditions, the majority of biopolymers have rather low activity [5], and the primary task in this area is therefore to create a science-based methodology for the synthesis of functional materials from polysaccharide having significant properties that can enhance their utilization on a practical scale. This is expected to open the possibility of a deeper understanding of the nature of intermolecular interactions in aqueous solutions of biopolymers. The optimal choice for a particular technology for engineering of polysaccharides can either be by chemical modification of using polymeric reagents [6] or by preparing composites [7]. A preview in literature [8–11] showed that research in the field of polysaccharide composite materials for water remediation has made some remarkable progress.

Considering biocompatibility, a polysaccharide with anticoagulant properties can increase its biocompatibility [12, 13]. Also, polysaccharides coated with

magnetite nanoparticles can be used for magnetic resonance imaging of liver tumours [14]. This is because they are hydrophilic, and when administered in approved conditions, are non-toxic.

Polysaccharides have specific functional chemical groups in their structure which make it easy to engineer them through the addition of reactive and bioactive groups to produce composites. For example, hydrogels of κ -carrageenan were chemically modified by carboxymethylation of the polymer chains and further coupled to an antibody for nano delivery applications [13].

In recent times, in adsorption design, numerous approaches have been geared towards the development of adsorbents containing natural polymers. Among these are polysaccharides such as chitin [15–17]; starch [18, 19] and their derivatives [20–24]. Their use in adsorption process has increased because of their unique structure, physicochemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains [25, 26]. Besides, the increasing number of publications on adsorption of toxic compounds by these natural polymers indicate that there is a recent interest in the synthesis of new adsorbent materials from polysaccharides.

Before the advent of chemical coagulants, the use of coagulants of natural origin has been acknowledged in indigenous water purification [27]. Antediluvian civilizations in Asia and Africa have used plant extracts and derivatives as a primary coagulant for water purification [28]. This has also been proven in the Sanskrit writings in India, dating back to 400 AD [27], and the Old Testament and Roman records, dating back to 77 AD [29]. With the invasion of synthetic chemical coagulants, traditional water clarification methods using natural coagulants were jettisoned, except in rural and developing countries, where access to the synthetic chemical coagulants are substantially limited [30]. Despite the wide acceptability and the conventional status of the synthetic chemical coagulants, the downsides manifested in the 1960s, when the negative impact on human and biota was profiled [31]. The other limitations with the use of the synthetic chemical coagulants include the relatively high costs of purchase, toxicity, large sludge volumes generation and considerable alteration of the pH of the treated water [32]. Furthermore, synthetic chemical coagulants that are based on organic polymers or polyelectrolytes have been reported to pose some environmental challenges, as some of the derivatives and byproducts are non-biodegradable and the intermediate products of their degradation are hazardous to human health, as their monomer is neurotoxic and carcinogenic [33].

2.2 Polysaccharide-based Coagulants

On the strength of the coagulating abilities exhibited by some materials of biogenic ancestries as coagulants in water treatment operations, multiplicities of green bio-based materials are continually being evaluated for their coagulating properties.

These biogenic coagulants have shown several advantages over the conventional synthetic chemical coagulants. For example, the sludge volume produced from the use of the green coagulants are much lower than that generated by the use of metal salts and the natural alkalinity of the water is not consumed during the coagulation process. Consequently, the natural coagulants have exhibited potentials that conferred on them the status of workable substitutes to synthetic chemical coagulants. The green biobased coagulants are biodegradable, safe to human health and have a wider effective dosage range for coagulation-flocculation (CF) of various colloidal suspensions. Since they can be locally grown, harvested and processed, they are usually cost effective, about the imported synthetic chemical coagulants.

An overview of the polysaccharide based coagulants (PBC) that have been investigated thus far showed that they ranged from the more widely known seeds of different plant species to bone shell extracts, bark resins and exoskeleton of shellfish extracts. A review of the research summary of twenty-one (21) types of plant-based coagulants, categorized as fruit waste and others, have been provided by Choy et al. [30]. The coagulating efficiencies of these natural materials, the barriers and prospects of commercialization were highlighted. A review of fourteen (14) plant-based natural coagulants, categorized as common vegetables and legumes has also been provided by [34]. The shortcomings of the prevailing research efforts in the use of natural coagulants were discussed to provide a platform toward the necessity for further research. To ensure comprehensive anecdote of green biobased coagulants, progress in natural polymeric coagulants, for water and wastewater purifications have also been documented by [35]. Viewpoints on the promise, limitations, and the findings on the use of these biobased coagulants were also documented.

The background information on selected polysaccharides that have been investigated as primary coagulants in water and wastewater treatment are presented in Table 2.1.

Consequent upon the glowing attributes of the PBC, it is pertinent that the underlying mechanisms of the coagulation efficiencies of these low cost, eco-friendly and pervasive coagulants should be understood to enable the users to exploit the process for optimal performance. To obtain relevant information for optimum and practical conditions for CF process, using PBC, there is the need to identify the active coagulating species, which ultimately determines the underlying coagulation mechanism of the process.

2.3 Overview of Active Coagulating Species in Polysaccharide-based Coagulants

Polysaccharides are polymers whose skeletal framework consist of monosaccharides and their derivatives. The skeletal framework could be either linear or branched, and they can contain only one type of monosaccharide (homopolysaccharides), or more (heteropolysaccharides). In CF operations, the macromolecular nature of the skeletal

Table 2.1 Background information on selected polysaccharides that have been investigated as primary coagulants

S/N	Scientific names	Common names	Family name	Country of origin	References
1	<i>Coccinia indica</i>	Ivy Gourd, Scarlet Gourd, Small Gourd, Kowai Fruit, Scarlet-Fruited Gourd	<i>Cucurbitaceae</i>	Central Africa, India and Asia	[36, 37]
2	<i>Hibiscus esculentus</i>	Okra, Lady's Finger, Gumbo, Gobo	<i>Malvaceae</i>	Old World tropics (West Africa)	[38]
3	<i>Luffa cylindrica</i>	Smooth Luffa, Egyptian Luffa, Vegetable Sponge, Sponge Guard	<i>Cucurbitaceae</i>	Old World tropics; probably Asia	[36, 38]
4	<i>Arachis hypogaea</i>	Peanut, Groundnut, Monkey Nut, Pinder, Goober	<i>Fabaceae</i>	South America	[36, 39, 40]
5	<i>Cicer arietinum</i>	Dal Seeds, Chick Pea, Bengal Gram, Garbanzo Bean	<i>Fabaceae</i>	Mediterranean region	[36, 41]
6	<i>Dolichos biflorus</i>	Horsegram, Kulthi	<i>Fabaceae</i>	Old World tropics	[42]
7	<i>Glycine max</i>	Soybean, Soya Bean	<i>Fabaceae</i>	Eastern Asia	[43]
8	<i>Guar gum</i>	Guar Bean, Cluster Bean, Guaran	<i>Fabaceae</i>	India	[44]
9	<i>Lablab purpureus</i>	Hyacinth Bean, Bonavist Bean, Chink, Country Bean, Dolichos Bean	<i>Fabaceae</i>	Old World tropics	[45]
10	<i>Phaseolus angularis</i>	Azuki Bean, Adsuki Bean, Red Bean	<i>Fabaceae</i>	Unknown Exact origin	[46]
11	<i>Phaseolus mungo</i>	Urad Bean, Black Gram, Black Lentil, Black Matpe, Urd Bean	<i>Fabaceae</i>	India	[36]

(continued)

Table 2.1 (continued)

S/N	Scientific names	Common names	Family name	Country of origin	References
12	<i>Pisum sativum</i>	Green Pea, Pea, Field Pea, Garden Pea, Stringless Snowpea	<i>Fabaceae</i>	Southwestern Asia	[36]
13	<i>Vigna unguiculata</i>	Cow Pea, Black Eyed-Pea, Southern Pea, Cowgram	<i>Fabaceae</i>	Southern Africa	[36]
14	<i>Phaseolus vulgaris</i>	Common Bean	<i>Fabaceae</i>	Central or South America	[40]
15	<i>Cereus repandus</i>	Cadushi, Giant Club Cactus, Hedge Cactus, Peruvian Apple Cactus	<i>Cactaceae</i>	South America	[47]
16	<i>Stenocereus griseus</i>	Pitaya agria, Sour Pitaya	<i>Cactaceae</i>	America	[48]
17	<i>Opuntia ficus indica</i>	Prickly pears, Tuna, Nopal	<i>Cactaceae</i>	Americas	[49–51]
18	<i>Oryza sativa</i>	Rice	<i>Poaceae</i>	China	[53]

framework is considered advantageous because it provides a significant number of active sites for particle adsorption and charge neutralization.

Generally, in the use of PBC, the ensuing elevation of the organic load of the treated water, which may result in the undesired and increased microbial activities, has been identified as a snag. To obviate this challenge, the coagulating active ingredients in the PBC are isolated from the total extract and the isolated coagulating fraction is used as such. In most cases, despite the successful isolations of the coagulating active ingredients, the proper identification of this active component has either been based on conjectural efforts shrouded in controversy [35]. Often, the identification of the coagulating active component of a particular PBC is based on reports from other researchers whose study material was entirely different from the PBC under investigation. Consequently, controversy often rages on the identity of the active coagulating species of most PBCs.

The active coagulating ingredients in PBC are polymeric in nature, but the molecular compositions and the skeletal framework of these polymers may vary from one PBC to another. Thus, the difference in molecular structures and framework is expected to influence the coagulation efficiency and the underlying mechanisms of coagulation of the PBC. An overview of the active coagulating species of the group of different PBC that have been investigated as a substitute to the conventional primary coagulants in CF operations is presented below, using the facts presented in various scientific reports as a guide.

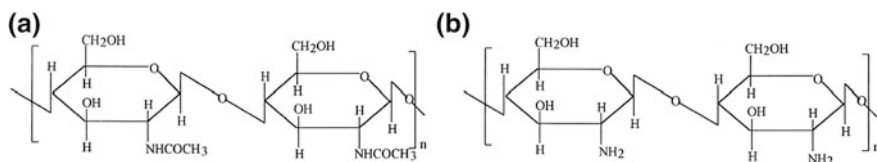


Fig. 2.1 Molecular units of Chitin (a) and Chitosan (b)

2.3.1 Chitosan

Among the array of investigated PBC for CF in the water industry, chitosan, is one of the most studied and has shown much promise. Chitosan is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine, produced by the deacetylation of chitin, a natural polymer of primary importance (Fig. 2.1).

Chitosan possesses both coagulating and flocculating properties (i.e., high cationic charge density, long polymer chains, bridging of aggregates and precipitation) in neutral or alkaline pH. Its uses are justified by its non-toxicity, biodegradability [27], and unusual chelation behaviour [54]. Thus, its unique physicochemical properties render it very efficient with regards to its interactions with various contaminants; including both particulate and dissolved substances.

The observed physicochemical features of chitosan have been ascribed to the intrinsic properties of amine functional groups (i.e. acid–base properties, solubility, cationic), which makes it to be very efficient for binding metal cations in near neutral solutions [55] and for interacting with anionic solutes in acidic solutions [55]. A peep into the acid–base properties of chitosan showed that the pK_a values of the amine groups strongly depends on the deacetylation degree of chitosan and the dissociation degree of the polyelectrolyte [56]. The pK_a of amine groups are close to 6.3–6.4, for entirely dissociated chitosan (with deacetylation degree close to 90%). This means that at pH 5, or below, more than 90% of amine groups get protonated. Hence, at pH below 5, most of the amine groups are protonated, and they can attract anionic species, but above the pH 5, the reverse is the case [57].

The coagulation efficiency of chitosan, in CF operations, was ascribed to the same characteristics highlighted above for adsorption reactions (i.e. cationic charge and ability to specifically bind to certain solid phases). It can effectively destabilize and coagulate natural particulate and colloidal materials, which are negatively charged, to promote the growth of large, rapid-settling floc than can then flocculate. This is because it is a long-chain polymer with positive charges (due to the high content of amine group).

2.3.2 Seed Gums

Gums are pathological products formed following an injury to plants or the effects of unfavourable conditions, such as drought, by the breakdown of cell walls.

Different seed gums have been used as eco-friendly and sustainable green PBC. It has been reported [58] that the polysaccharide composition of mature endosperm cell walls contained three mannan groups: pure mannans; glucomannans and galactomannans. An overview of the constituents of the different seed gum coagulants showed that the active coagulating component is a water-soluble, macromolecular, hydrocolloids, galactomannans, having galactose and mannose in 1:2 molar ratio (Fig. 2.2a). Galactomannans are related to mannans but contain more

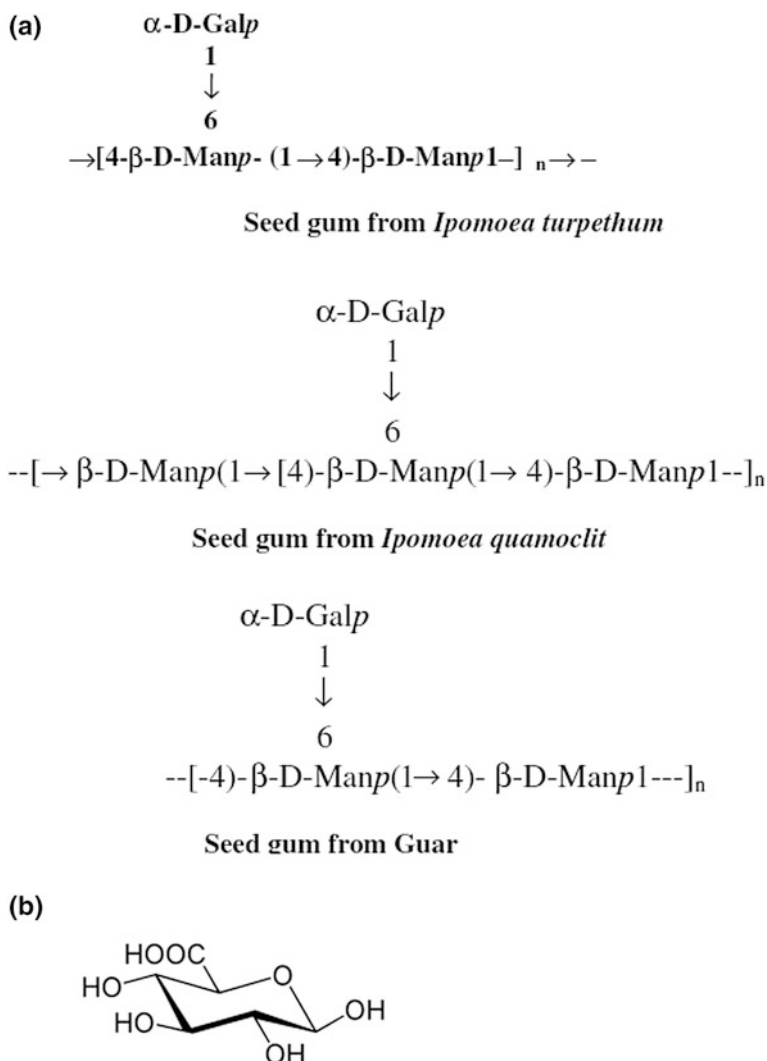


Fig. 2.2 **a** Representation of the chemical structures of different Galactomannans. **b** Chemical structure of Uronic acid (Glucuronic acid)

(1,6)- β -D-galactosylside chains. These seed gums are reported [59] to consist of a linear chain of β (1 \rightarrow 4) linked mannopyranosyl units with D-galactose side chains, attached through α (1 \rightarrow 6) linkage to the main chain. However, they differ in their fine structure, like molecular weight and degree of polymerization.

Galactomannans with a high degree of side chains are soft and highly hydrophilic. They have been reported to be present in the endospermic leguminous seeds, such as fenugreek (*Trigonella foenum-graecum*), guar (*Cyamopsis tetragonoba*) and locust bean (*Ceratoniasiliqua*), in the endosperm of tomato (*Solanum lycopersicum*) and coffee seeds (*Coffea arabica*), and other groups such as *Convolvulaceae*, *Asteraceae* and *Arecaceae* [58]. The presence of galactomannans has also been reported in many subfamily species including *Cassia*, *Senna*, *Leucaena*, *Mimosa*, *Prosopis*, *Bowdichia*, *Crotalaria*, and *Indigofera* [60]. Besides, the presence of galactomannans has been reported in cotyledons and hull of *Lapinus albus* [61].

The presence of an active coagulating component of the seed gum of *Sterculia lychnophora* (i.e. Malva nut seed or Taiwan sweetgum tree), whose properties are similar to uronic acids has also been reported [62]. Uronic acids (Fig. 2.2b) are a class of sugar acids with both carbonyl and carboxylic acid functional groups. They are sugars in which the terminal carbon's hydroxyl group has been oxidized to a carboxylic acid. It was posited that the high molecular weight and the presence of uronic acid by this seed gum are the requirements for the bridging and adsorption mechanism in CF operations. It was noted that the molecular weight and the intrinsic viscosity of the *S. lychnophora* seed gum were much higher than that of many polysaccharide gums (i.e., guar gum, locust bean gum, and pectin) that are currently available in the market [62].

2.3.3 Fruit Wastes

An overview of different research reports showed that extracts of an array of fruit wastes had been studied as coagulants in the treatment of turbid synthetic water, raw surface water and wastewater [30]. These fruit wastes include the seeds of *Carica papaya*, *Feronia limonia*, *Mangifera indica*, *Persea americana*, seeds and pollen sheath of *Phoenix dactylifera*, *Prunus armeniaca*, *Tamarindus indica*, the peels of *Citrus Sinensis* and the foliage of *Hylocereus undatus*.

The coagulating actions of these fruit wastes were ascribed mainly to the presence of proteins and polysaccharides, which are among the natural polymers present in fruit waste. The nomenclature of the particular polysaccharide that is responsible for the coagulating properties of the fruit waste is often not identified or pinpointed. The usually large molecular weights and longer polymeric chain of polysaccharides are typically regarded as the impetus for coagulation efficiency since the number of active sites that are available for particle adsorption, and subsequent flocculation abounds in such skeletal frameworks.

2.3.4 Mucilage

Mucilages are normal products of metabolism, formed within the cell (intracellular formation) and they are produced without injury to the plant. It is a thick, gluey substance produced by nearly all plants and some microorganisms. It is a polar glycoprotein and an exopolysaccharide. Mucilage in plant plays a role in the storage of water and food, seed germination, and thickening of membranes. Cacti and flax seeds are rich sources of mucilage. The mucilages of *Opuntia ficus-indica* cactus, *Hibiscus esculentus* (okra), *Plantago species*, *Malva sylvestris* (mallow) have been tested, as primary coagulants in CF operations. These plants are characterized by the production of a hydrocolloid (i.e. mucilage) which forms molecular networks that can retain significant amounts of water [63]. According to [64], the hydrocolloids are complex polymeric substances of carbohydrate nature, with a highly branched structure. It contains varying proportions of L-arabinose, D-galactose, L-rhamnose, and D-xylose, as well as the galacturonic acid in different proportions.

In *O. ficus-indica*, the mucilage structure is proposed as two distinctive water-soluble fractions. One inspection with gelling properties with Ca^{2+} and the other is mucilage, without gelling properties [65]. Majdoub et al. [66] reported that in *O. ficus-indica*, the water-soluble polysaccharide fraction with thickening properties represents less than 10% of the water-soluble material. By a working hypothesis that coagulation occurs through a polymer bridge, the polysaccharide, presenting *Opuntia* spp., are considered as the active coagulating ingredients.

In order to identify the active coagulating ingredient, in the mucilage of *Opuntia* spp., individual mucilage components (D, L-arabinose, >99%; D-(+)-galactose, >99%; L-rhamnose, >99%; and D-(+)-galacturonic acid, >97%), were tested independently and in combination [67]. It was observed that the galacturonic acid component of the mucilage might be responsible for some of the turbidity reduction by *Opuntia* spp. Galacturonic acid, added independently, was able to reduce turbidity by more than 50%. Regardless, arabinose, galactose, and rhamnose displayed no coagulation activity, however, when added in combination with galacturonic acid, they reduced turbidity between 30 and 50%. The individual mucilage components, in isolation and combination, could only account for 50% of the turbidity removal observed when the full cactus pad was introduced to the turbid water solution. Consequently, it was concluded that there are additional components of the *Opuntia* spp., beyond those found in the mucilage, contributing to the observed coagulation activity. Further studies were recommended to determine the other components of the *Opuntia* spp. plant contributing to coagulation.

2.3.5 Plant Seed Extracts

The coagulation efficiency of natural coagulants, derived from the seeds of Nirmali and maize [68] mesquite bean and *Cactus latifaria* [47], *Cassia angustifolia* [69]

and different seeds of leguminose species [70] have been reported. Horse chestnut (*Aesculus hyppocastanum*) from family *Sapindaceae*, and Common oak (*Quercus robur*), Turkey oak (*Quercus cerris*), Northern red oak (*Quercus rubra*) and European chestnut (*Castanea sativa*), from family *Fagaceae*, have also been studied as natural coagulants [71] in CF operations. Amongst the different seeds that have been investigated as PBC, the seed of *Moringa Oleifera* (MO) has received the greatest attention and the coagulation efficiency is often used as a baseline for the evaluation of the other PBC. On the assumption that the active coagulating species in MO is a protein, it is assumed that the active coagulating species in other seed coagulants are also proteins.

The coagulant components of the water extracts of MO has been described as a water-soluble protein with a net positive charge [72] and as dimeric cationic proteins with molecular mass of 12–14 kDa and isoelectric point (pI) values that ranged between 10 and 11 [73]. It has also been posited that the coagulating MO extract possesses a molecular mass of 6.5 kDa and a pI value greater than 10 [74]. On the other hand, it was reported that the active component from an aqueous salt extract was not a protein, polysaccharide or lipid, but an organic polyelectrolyte with a molecular weight of about 3.0 kDa [75]. It could be assumed that the nature of the water and salt extract of the coagulating species in MO seed may be different based on the different reports. In another study, the active coagulating components of MO was reported to be soluble cationic proteins and peptides, with a molecular weight ranging from 6 to 16 kDa and isoelectric pH values around 10 [74]. One of these peptides, named MO2.1, has been purified, sequenced and proven to exhibit coagulating activity on a glass powder suspension [74], bacteria and clay [76]. A non-protein component, with a molecular weight of 3 kDa has also exhibited coagulating activity in kaolin suspension [77, 78]. The isolation of a large molecular mass protein fraction, approximately 66 kDa, that exhibit coagulation activity has also been reported [79]. Consequent upon the different opinion on the nature and properties of the coagulant protein from *M. Oleifera*, more studies are being carried out to unravel the nature of the actual coagulating species in the MO seed extracts.

2.3.6 Polyphenolics

Complex polysaccharide tannin derivatives have been used in potable water and industrial effluent treatment applications [80]. The use of tannin as either the primary coagulant or coagulant aid for water treatment have been reported [80–85]. Tannins are mostly vegetal water-soluble polyphenolic compounds with a molecular weight that ranged between 500 and some thousand Daltons. Polyphenols are a structural class of mainly natural, but also synthetic or semisynthetic organic chemicals characterized by the presence of multiples of phenol in the structural units. The number and characteristics of the phenol structures underlie the unique physical, chemical, and biological (metabolic, toxic, therapeutic, etc.) properties.

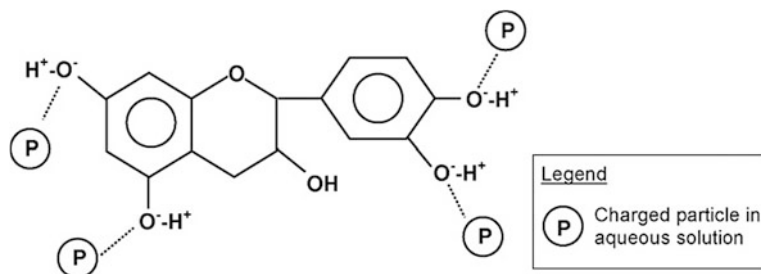


Fig. 2.3 Schematic representation of basic tannin structure in aqueous solution and possible molecular interactions [84]

The presence of phenolic groups in tannin clearly indicates its anionic nature, since it is an excellent hydrogen donor. The schematic representation of primary tannin structure, in aqueous solution, and possible molecular interactions that induce coagulation are presented in Fig. 2.3 [86].

Phenolic groups get deprotonated readily to form phenoxide, which is stabilized via resonance. This deprotonation is attributed to the delocalization of electrons within the aromatic ring, which increases the electron density of the oxygen atom. This provides an indication that the more the phenolic groups that are available in a tannin structure, the more efficient is its coagulation capability. An interesting study on the application of a commercial tanning containing both amine and phenolic groups for water treatment [87] showed that this tannin is cationic in nature since there is a single tertiary amine group per monomer, giving a charge density of approximately 3 meq/g. This tannin also exhibits amphoteric nature because of the presence of phenolic groups.

2.3.7 Starch

Starch and starch rich materials (e.g. cereals) have also been studied as primary coagulants [88, 89] and coagulant aid [90] in CF operations. In the crude form, starch consists of a mixture of two polymers of anhydroglucose units, amylose and amylopectin [91]. Amylose is a linear polymer of 1–4 linked α -D-glucopyranosyl units with low molecular weight, which makes up 25% of the starch while the rest is amylopectin, a highly branched polymer of α -D-glucopyranosyl residues linked together by 1–4 linkages with 1–6 bonds at the branch points. As a major component for most starches, amylopectin plays a critical role in defining the characteristics of the starch.

Albeit, different reports have been presented on the coagulating effects of starch in water treatment, but [35] opined that the poor cationic charge density of starch couldnot make it an efficient primary coagulant. The poor coagulating ability of starch and the constituents (i.e. amylose and amylopectin) has also been ascertained

by Rath and Singh [92]. The flocculation characteristics of grafted and ungrafted starch, amylose, and amylopectin were studied, and it was observed that the behaviour of amylose could not be considered because of its insolubility in water. In cases of starch and amylopectin, there was practically no floc formation, which may be the reason for the poor flocculation efficiency exhibited [92].

Consequent upon the different reports on the poor coagulation efficiencies of the starch-based materials, it could be concluded that adsorption (a surface phenomenon) was possibly mistaken for coagulation (a phase transformation reaction) in the published reports on the use of starches derived from various sources, as primary coagulants. An overview of the applications of starches in CF operations showed that to enhance the surface charge density of starch molecules, it is modified to obtain products of excellent coagulation efficiency.

2.3.8 *Actinobacteria*

Coagulants of microbial origin referred to as bioflocculants, are innocuous, environmentally friendly and have been documented to show flocculation efficiency that is comparable to those of conventionally used flocculants [93–95]. Microbial flocculants are mainly polysaccharide produced mostly by bacteria such as *Alcaligenes cupidus* KT-201 [96], *A. latus* B-16 [97], and *Bacillus* sp. DP-152 [98]. Axenic cultures including *Bacillus firmus* [99], *Arthrobacter* sp. Raats [100], *Enterobacter cloacae* WD7 [101], *Streptomyces* sp. Gansen and *Cellulomonas* sp. Okoh [95] *Bacillus* sp. Gilbert [102] and *Pseudoalteromonas* sp. SM9913 [103], of the extreme deep sea psychrophilic milieu, have been respectively shown to produce bioflocculants. High production cost and low yield have been attributed to the limited application of bioflocculant in water treatment operations [104].

The bioflocculants produced from *Streptomyces* sp. Gansen and *Cellulomonas* sp. Okoh were characterized as proteoglycan and glycosaminoglycan polysaccharide, respectively, and were found to be stable to extremes of pH and high temperature [105]. Chemical analyses of the purified consortium bioflocculant revealed that polysaccharides (34.4%) and proteins (18.56%) accounted for about 52.96% of the composition. Further, analysis of the polysaccharide constituent showed the presence of neutral sugars (5.7 mg), amino sugars (9.3 mg), and uronic acids (17.8 mg), out of 100 mg of the purified bioflocculant.

The determination of the component of a partially purified *E. cloacae* WD7 biopolymer showed that it was composed of neutral sugars (29.4%) and uronic acids (14.18%) as the major and minor components, respectively, with a little amount of amino sugar (0.93%) [101]. Neither alpha amino acids, analysed by the ninhydrin reaction (L-leucine standard), nor aromatic amino acids, analysed by the Xanthoproteic reaction using L-tryptophan standard [106] were detected. This showed that it contained no amino acids or protein in its molecule, hence, the biopolymer produced by *E. cloacae* WD7 was classified as a polysaccharide.

The uronic acid contained in its molecular structure might be glucuronic acid, or galacturonic acid is generally found in the acidic polysaccharides [107].

The determination of the electric charge on the biopolymer was carried out via the addition of cetylpyridinium chloride (CPC) to the solution of partially purified biopolymer of *E. cloacae* WD7. The formation of precipitate indicated that it contained acidic groups in its structure due to the interaction with the quaternary ammonium cation (QN^+) of the CPC, resulting in the formation of a cetyl pyridinium chloride polysaccharide complex [108]. Therefore, this polymer was classified as an acidic polysaccharide; its component acid can be one or more of the acidic groups of pyruvate, succinate, uronate, acetate or sulphate [109, 110]. Margaritis et al. [107] surmised that these acidic groups may be responsible for the anionic (or acidic) charge of the polysaccharide.

2.3.9 Alginate

Alginate (chemical formula: $(\text{C}_6\text{H}_8\text{O}_6)_n$), is the term usually used to refer to the salts of alginic acid, and alginic acid itself. It is an anionic polysaccharide that binds with water to form a viscous gum. Alginates occur both as a structural component in marine brown algae (*Phaeophyceae*), comprising up to 40% of dry matter, and as capsular polysaccharides in soil bacteria. Alginates from different species of brown seaweed show variations in their chemical structure and physical properties. Alginic acid is the only polysaccharide, which naturally contains carboxyl groups in each constituent residue, and possesses various abilities for functional materials [111]. It is a linear copolymer with homopolymeric blocks of (1-4)-linked β -D-mannuronate (M) and its C-5 epimer α -L-guluronate (G) residues, respectively, covalently linked together in different sequences or blocks. The monomers can appear in homopolymeric blocks of consecutive G-residues (G-blocks), consecutive M-residues (M-blocks) or alternating M and G-residues (MG-blocks). Therefore, the knowledge of the monomeric composition is not sufficient to determine the sequential structure. Haug and Larsen [112] suggested that a second-order Markov model would be required for a general approximate description of the monomer sequence in alginates. The main difference, at the molecular level, between algal and bacterial alginates, is the presence of O-acetyl groups at C_2 (carbon in the second position) and C_3 (carbon in the third position) in the bacterial alginates [112].

The most useful and unique property of alginates is their ability to react with polyvalent metal cations, especially calcium ions to produce stable gels or insoluble polymers [113, 114]. The mechanism of coagulating action of alginate is assumed to be guided by either charge neutralization, along with bridging the gap between the particles, or by the formation of calcium alginate gel, which is especially more efficient at high calcium concentrations [115]. Calcium alginate gel combines with particles and captures (i.e. sweep coagulation mechanism) them at the stage of gel formation or after gel formation. Finally, floc formed by the gel and the particle gets dense enough and settles down [116].

2.4 Underlying Mechanisms of Coagulation-Flocculation Process

On the strength of the classifications proposed by [117], the coagulation or destabilization of suspended colloidal particles in a system is postulated to be achieved via four mechanisms, namely the double-layer compression, charge neutralization, bridging as well as sweep coagulation. The occurrence of this mechanism of coagulation is a function of the type of coagulant used and the nature of the water matrix on which coagulation is to be performed. Any of these modes of coagulation reaction can occur singly or in combination. The synopsis of the underlying principle of each mechanism of CF is presented below:

2.4.1 *Double-Layer Compression*

This coagulation mechanism relies on the action of an excess electrolyte (a highly charged ionic species), added as a coagulant to the aqua system. The coagulant alters the overall ionic concentration of the system and the electrical double layer, surrounding the particulate, is compressed to the extent that the repulsive energy barrier between the particulates is lowered. This phenomenon promotes molecular attraction and subsequent micro and macro flocs formation. However, the effectiveness of this coagulation mechanism is questionable and is usually not preferred. The presence of bivalent ions (e.g. Ca^{2+} and Mg^{2+}) in water has been reported to induce some form of coagulation activities via the double-layer compression mechanism [118].

2.4.2 *Charge Neutralization*

This involves the adsorption of oppositely charged ionic species, present in the coagulant, on the colloidal surface. Under normal surface water conditions, colloidal particles are usually negatively charged, thus, positively charged coagulants are attracted to the colloids to induce surface charge neutralizations. The effectiveness of this mechanism is strongly dependent on the coagulant dosage introduced because particle stabilization could easily occur once the optimum dosage is exceeded.

2.4.3 *Adsorption and Bridging*

The bridging of particles occurs with the introduction of long-chain polymers or polyelectrolytes, as the coagulants. The coagulants are capable of extending into the solution to capture and bind multiple particulates together.

2.4.4 Sweep Coagulation

Sweep coagulation occurs through the precipitation of metal hydroxide, and the colloidal particles got enmeshed in these precipitates. Sweep coagulation could result in improved coagulation for greater removal performance in comparison with charge neutralization [119]. Consequent upon the fact that higher coagulant dosage is required for this mode of coagulation mechanism to take effect, large sludge volume has generated at the end of the coagulation process.

An inference could be drawn that a specific coagulant can only operate using some but not all the modes of coagulation mechanism judging from the principle of each of the coagulation mechanism highlighted above. For example, alum coagulants (aluminium or ferric) can only operate using sweep coagulation, charge neutralization or double layer compression, singly or in combination, but cannot operate using the adsorption and bridging mechanism. In the same vein, coagulants based on polyelectrolytes cannot operate using sweep coagulation, but it can operate with adsorption and bridging, double layer compression or charge neutralization.

2.4.5 Insight into the Coagulation Mechanism of PBC

Consequent upon the dependence of the operating coagulation mechanism, in a specific CF system, on the nature of the coagulants and the water matrix, the PBC may not function via similar underlying coagulation mechanism. Thus, it is recommended that the underlying mode of CF process should be evaluated, contextually, to obtain an informed opinion.

An overview of the proposed mechanisms of CF that has been reported by different researchers (e.g. [62, 67, 120–122] etc.), when PBC is used as the primary coagulant, showed that the adsorption and bridging coagulation and charge neutralization are the mechanisms that are usually pinpointed. Using chitosan as a case study of PBC, it has been posited that the CF ability occurs through a dual mechanism. These include coagulation by charge neutralization and flocculation by bridging mechanism. Since Chitosan is a polymer with moderate to high molecular weight and it is positively charged within the pH of natural water, it can effectively coagulate natural particulate and colloidal materials, which are negatively charged, through adsorption, charge neutralization and interparticle bridging. The coagulating ability of other PBC, whose genre were delineated in sects. 2.3.1–2.3.9, have also been ascribed to this same mechanism, because of the macromolecular nature of the skeletal framework of the active coagulating species in PBC.

A comprehensive account of the process of CF mechanism, via the adsorption and bridging (Fig. 2.4) and charge neutralization mechanism, by polymeric coagulants was described by [121].

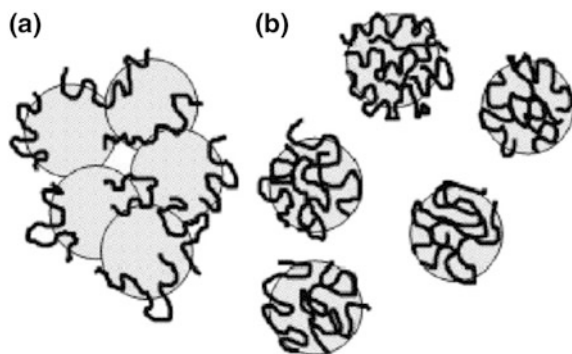


Fig. 2.4 Schematic representation of **a** an adsorption and bridging coagulation mechanism **b** restabilization by adsorbed polymeric coagulant chains [121]

It was posited that the adsorption of particulates in an aqua matrix on the polymer surface occurs only if an affinity exists between the coagulant polymer framework and the dispersed colloidal particle surface in the aqua matrix. The adsorption affinity must be sufficient to outweigh the loss of entropy associated with polymer adsorption since an adsorbed chain will have a more restricted configuration than a random coil in free solution [123]. Depending on the nature of charge on the active coagulating species in the PBC, the adsorption interaction could occur via electrostatic interaction, hydrogen bonding and ion binding. An essential requirement for bridging flocculation is that there should be sufficient unoccupied surface on a particle for attachment of segments of polymer chains adsorbed on other particles. It follows that the adsorbed amount should not be too high, else the particle surfaces will become so highly covered that there are insufficient adsorption sites available and the particles are said to be restabilised (Fig. 2.4b). It is also noteworthy that, the adsorbed amount should not be too little; otherwise not enough bridging contacts could be formed. These considerations lead to the idea of an optimum dosage bridging flocculation.

Polymer bridging gives much stronger aggregates (flocs) than those formed in other ways i.e. by metal salts [123]. This is clearly evident by the common observation that large flocs can be formed long-chain polymers even under conditions of enough high shear, as in a stirred vessel. The flocs usually grow to equilibrium (steady state) size, which is dependent on the applied shear or stirring speed. The stronger the flocs, the larger they can grow under given shear conditions [124]. Bridging contacts are also more resistant to breakage at elevated shear levels. However, floc breakage can be irreversible, so that broken flocs do not quickly re-form under reduced shear conditions [125]. Irreversible breakage may be due to scission of polymer chains under rough conditions [126] or the detachment of adsorbed polymer segments followed by re-adsorption in a manner less favourable for bridging interactions.

Most often, particulates and colloidal fractions in water matrix are negatively charged. Thus PBC whose active coagulating ingredient is cationic would be most effective as a coagulant. Electrostatic interaction gives high adsorption in such

system, and the neutralisation of the particle surface and even charge reversal can occur. Thus, the possibility that coagulation could occur simply as a result of the reduced surface charge of the particles and hence a decreased electrical repulsion between them is very high. In CF operations, the optimum coagulation is achieved at coagulant dosages that are required to simply neutralise the particle surface charge, or to give a zeta potential close to zero [127]. PBC of high charge density are more effective, only because, for a given dosage, they deliver more charge to the particle surface. Since high charge density polymers tend to adsorb in a rather flat configuration, there is little opportunity for bridging interactions [123].

When high charge density PBC adsorb on negatively charged surfaces with a relatively low density of charged sites, another possibility arises, which has become known as the “electrostatic patch” mechanism [128, 129]. An important consequence of “patchwise” adsorption is that, as particles approach closely, there is an electrostatic attraction between positive patches and negative areas, which can give particle attachment and hence coagulation. Floccs produced in this way are not as strong as those formed by bridging, but stronger than floccs formed in the presence of metal salts or by simple charge neutralisation. Re-flocculation after floc breakage occurs more readily in the case of an electrostatic patch than bridging [125].

2.5 Conclusion

The active coagulating species in PBC varied widely, and the underlying mechanisms of coagulation is a function of the skeletal features of the PBC and the water matrix composition. Adsorption, charge neutralization and bridging mechanism are the coagulation-flocculation mechanism that is common in this class of coagulants.

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