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Advancements in natural bio-flocculants for water treatment

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Abstract

Natural polysaccharides, derived from biomass feedstocks, marine resources, and microorganisms, have been attracting considerable attention as benign and environmentally friendly substitutes for synthetic polymeric products. Besides many other applications, these biopolymers are rapidly emerging as viable alternatives to harmful synthetic flocculating agents for the removal of contaminants from water and wastewater. In recent years, a great deal of effort has been devoted to improve the production and performance of polysaccharide bio-based flocculants. In this review, current trends in preparation and chemical modification of polysaccharide bio-based flocculants and their flocculation performance are discussed. Aspects including mechanisms of flocculation, biosynthesis, classification, purification and characterization, chemical modification, the effect of physicochemical factors on flocculating activity, and recent applications of polysaccharide bio-based flocculants are summarized and presented briefly.

Keywords: Bio-flocculants, chitosan, tannins, gums, mucilage, sodium alginate, cellulose

Full length article **Corresponding Author*, e-mail: farwa668@gmail.com

1. Introduction

Flocculants are used as additives in a wide range of industrial applications, including water and wastewater treatment, food and beverages, mining, dyes and textile, and fermentation and its downstream processing. Flocculants bring colloidal and other particles suspended in a liquid together to form larger particles (or flocs) for promoting the settling of these particles from the stable suspension. Therefore, they have been extensively applied for removing turbidity, suspended and dissolved solids, colors and dyes, and chemical oxygen demand (COD) in sedimentation and clarification processes [1-7]. Bio-flocculants are biodegradable polymers and safer in contrast to chemical ones. Natural organic flocculants originated from natural polymers and polysaccharides are environment-friendly in nature. They can be easily obtained from reproducible agricultural sources and are favorable as they do not produce secondary pollution and are shear stable [8-16].

2. Types of Bio-Flocculants

2.1. Chitosan

Chitosan is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine, produced as a result of deacetylation of chitin. Chitin is the second most abundant biopolymer in the world after cellulose. It is considered as natural polymer of significant importance [17]. Chitosan has special characteristic properties as compared to all other biopolymers because of the primary amino groups. Chitosan has high nitrogen percentage than cellulose and therefore it is substantially important commercial compound. Major sources of chitosan include the marine crustaceans, crabs and shrimps [17]. Numerous factors are responsible to alter the properties and characteristics of chitosan. Main factors include degree of deacetylation, crystallinity, molar amounts of deacetylated groups and molecular weight of compounds [18]. Chitosan has numerous applications in the fields of dentistry, ophthalmology, chemistry, biomedical engineering, agriculture, textile industry, pharmacy, pulp and paper, cosmetics, oenology, biotechnology, food factories and photographic industries [19-20].

Chitosan can be conditioned and potentially used in wastewater recovery procedures (Table 1). Chitosan can be utilized for pollutant complexation in variable types, for example water soluble fibers and membranes for adsorption of the different types of pesticides, organic pollutants and other dyes [21-22]. Bio-polymeric chitosan commonly used in gel-bead type, for adsorption in fixed bed and batch column systems. Ceramic is commonly deposited and used as a support to form gel bead. Chitosan is used to improve ultrafiltration mechanism and extraction process in water soluble forms [22-23]. It also has many unique characteristic properties which makes it an effective coagulant as well as flocculent for the elimination of pollutants and dissolve particles present in the wastewater [22].

Chitosan exhibits very unique behaviors; it can act as a flocculent as well as coagulant, i.e. long polymeric chains and aggregates bridging, high cationic charge density and precipitation (basic or neutral pH). It has many beneficial characteristics which can be explained by its uses like (a) the extraordinary chelation behaviors [24] (b) its non-toxicity and biodegradability [21-25-26]. The physicochemical properties of chitosan explained its high efficiency during interaction with dissolve substances and suspended particles. Such favorable characteristics of chitosan are utilized to design the coagulation-flocculation treatment methods in order to use them for elimination of different pollutants (Table 2).

Chitosan is successfully used in flocculation at pH above pKa values of the macromolecule and to treat minerals for coagulation of contaminants carrying negative charge in acidic media containing either humic acid or dye molecules for organic solutions [24-27-29]. By adding chitosan, floc size can be increased thereby lowering setting rate. It has several drawbacks for example (i) variable chitin and chitosan sources are employed during coagulation-flocculation (ii) it is effective over short pH range and (iii) biopolymer chitosan has characteristic variability and heterogeneity that causes variation in coagulation behavior. Chitosan is featured on basis of crystallinity, polymer weight and fraction of deacetylation as all given parameters significantly affect its physicochemical properties like solubility and viscosity [25].

Chitosan is described as a rigid structure of linear hydrophilic copolymer, composed of glucosamine units as well as acetyl glucosamine groups. Solubility is one of the most important aspects that is difficult to control while designing an experimental setup [18]. Chitosan is insoluble in water as well as organic chemicals. Although, in dilute organic acids like formic acid, acetic acid and inorganic acids (excluding sulphuric acid), free amino groups are protonated and the biopolymer becomes fully soluble [18]. Solubility of chitosan is mainly based on numerous components, for example molecular weight, concentration of acid required to dissolve polymer, degree of deacetylation (DD), division of acetyl groups along with macromolecular chain, polymer concentration and ionic strength.

2.2. Tannin

Tannin is described as polyphenolic chemical compound which functionalizes to merge different other organic components, for example proteins, alkaloids, amino acids and causes their precipitation. Tannins are water soluble species mainly vegetal in nature with molecular weights ranging from 500 to several thousand Daltons. They are wide spread in many plants species due to their vital role in regulation of plant growth and in providing protection from predators. Sources of tannin include *Acacia mearnsii de Wild* (Black wattle) and *Castanea sativa* (Chestnut). The structure of tannins cannot be described very accurately as they are chemically complex species [30]. Sometimes, alum is merged with tannin. It is used to lower the amounts of optimum dose of alum required and the flocs obtained are coarser leading to rapid settling of particles [7]. When the tannin derived from waste walnut husk is combined with alum, it is effectively employed for elimination of color from synthetic metal ions, for eliminating metal ions from polluted water. Higher quantities of metal ions can be isolated by using relatively less concentration of alum and tannin coagulant dosage. Moreover, color is imparted by tannin in contrast to using alum alone [31]. It was concluded from FTIR results that –OH group of the tannin, is involved in interaction with metal ions [32].

2.3. Gums and Mucilage

Around many regions of globe for wastewater recovery, natural coagulants are utilized as common practice. As compared to conventional organic polymers used in wastewater recovery, gums and mucilage offer safe alternatives. They have many characteristic properties favorable to environment and beneficial to human health. The plants based industrial units that emerged in India and Sudan played an effective role in economic prosperity belonging to the family Leguminosae i.e. seed of *Cyamopsis tetragonolobus.* The galactomannan, sometimes also known as "guar gum" is also used all over the world due to its potential advantages. Guar gum is widely cultivated in Sudan throughout gum Arabic belt which is extended from West to East. United States Public Health Service approved guar as coagulation aid merged with ferric sulfate, lime and alum in wastewater treatment. The use of guar is favored as it stimulates size of floc, thereby increasing the setting rate of impurities, raise time between back washes and lower solid carried over to Walters. Seeds of galactomannans, as whole seeds of genera Leguminosae family are industrially very important as they are very famous for coagulation and decolorizing textile wastewater.

Plant species such as *Trigonella foenum-graecum* (Fenugreek), *Plantago ovata* (Isabgol), *Hibiscus* (famous economical sudanese crop)*/Abelmoschus esculentus* (Okra) and *Tamarindus indica* (Tamarind) are also some of the potential adsorbents that provides safer alternative to conventional adsorbents for wastewater treatment. *Plantago psyllium* (Psyllium) and *Malva sylvestris* (Mallow) produce mucilage in appreciable amount. They are basically derived by using precipitation with drying and alcohol along with aqueous extractions. They are very beneficial in contrast to sewage water processing, textile pollutants, tannery effluents, landfill leachate and biologically treated effluents [24]. These studies reported the data for elimination of contents upto 70% removal of turbidity, 90% color elimination, 60% reduction of COD and 85% removal of TSS. An average of >85% suspended solids removal from tannery effluent and sewage wastewater was gained using 0.08 mg/L of Fenugreek mucilage and okra gum about 0.12 mg/L, respectively. In addition, flocculation efficiency of these bioflocculants was discovered to be almost equivalent with synthetic polyacrylamide. In contrast to synthetic flocculants in terms of efficiency, majority of them are effective in low concentration [33-34].

2.4. Sodium Alginate

Sodium alginate is water-soluble salt of alginic acid. It is linear anionic polymer and commercially very important. Sodium alginate has an average molecular weight of 500,000 [35]. Numerous commercially available water soluble salts include potassium alginate and ammonium alginate whereas calcium alginate and alginic acid are examples of water insoluble forms. Sodium alginate is insoluble in cold water. Propylene glycol alginate is known as one of the most substantial commercial grade organic polymer. Brown green algae (phaeophyceae) and sea weeds are principal sources of sodium alginate. It binds almost 200-300 turn weight of water in order to produce gel. Sodium alginate has numerous applications in food industry as marmalades, thickeners in ice cream and fruit jellies etc. Propylene glycol esters of alginic acids are beneficial as foam stabilizers. A great deal of scientific study focuses on sodium alginate and its derivatives. Polyacrylamide grafted sodium alginate flocculent has been indicated very recently [36].

2.5. Cellulose

Cellulose and its derivatives are most abundant biopolymers all around the globe that are nevertheless still rare. Aqueous periodate oxidation process is used as one of the finest method of producing cellulosic flocculent. During the process, reactive aldehyde characteristics are introduced into cellulose [37-38]. Aldehyde groups of 2,3-dialdehyde cellulose (DAC) are easily and selectively converted into various functional groups including carboxylic acids, sulphonates and imines [39-42]. In the flocculation of kaolin suspensions using anionic and cationic cellulose derivatives, favorable results were deduced [43]. It was concluded that anionic cellulose nano particles reported fairly enhanced flocculation ability as compared to fully water soluble derivatives [43-44].

2.6. Moringa

Trees of *Moringa oleifera* are the most widely exploited species of Moringa and proteins extracted from its seeds have been identified as the most efficient natural coagulant for water purification. Most common species is *Moringa oleifera* indigenous to India and widely cultivated in Sudan.

3. Graft Flocculation/Copolymerization

Graft copolymers are adequately synthesized by grafting polyacrylamide chain or poly (2-methacryloyloxyethyl) trimethyl ammonium chloride onto cellulose, sodium alginate, agar, starches, oatmeal and chitosan [45-49]. The flocculating properties of graft copolymers were examined for the treatment of effluents emitted by municipal sewage, raw mine, textile industry and pulp mill. It was reported that molecular weights of graft copolymers in aqueous solution are responsible for flocculating properties. Moreover, one of the characteristic properties of graft copolymers is the presence of fewer and longer dangling polymer chains with high branched structure and a high molar mass. This give graft copolymers easy accessibility to impurities residing in effluent and therefore claimed to be effective flocculating agents at low concentration [8-50]. The greater flocculation efficacy corresponds to higher radius of gyration or higher hydrodynamic volume of the macromolecule [51]. Higher intrinsic viscosity is because of high percentage of grafting. High flocculation efficiency is due to higher intrinsic viscosity. Different grades of poly-methyl methacrylate grafted *psyllium* (Psy-g-PMMA), while (Psy-g-PMMA 3) grade having highest percentage of grafting has reported maximum efficiency of flocculation. In contrast to raw materials (*psyllium*), grafted *psyllium* provides improved performance in flocculation [50-52].

4. Mechanism to Coagulation-Flocculation

4.1. Coagulation Mechanism

One of the major causes of attractive and repulsive forces like electrostatic forces, van der waals forces and Brownian movement, is due to stability and instability of suspended particles. The process of coagulation has both physical and chemical nature. Coagulants and particles react to produce aggregates followed by subsequent sedimentation as shown in Fig 1. When negatively charged colloids are neutralized by cationic coagulants, spongy mass termed as "microfloc" is formed. The overall process of coagulation takes place in two steps i.e. particle aggregation and charge neutralization.

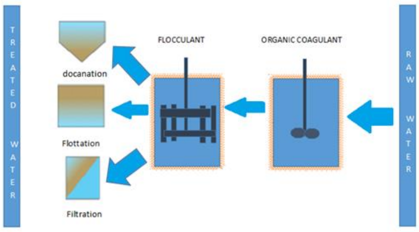

Figure 1: Treatment process of coagulation/flocculation

4.2. Mechanism for Chemical Coagulation

Coagulation takes place by adding various types of coagulants for example salts of aluminum such as aluminum sulphate; salts of iron such as ferric chloride, ferric sulphate and all corresponding polymers into the water. The above mentioned chemical coagulants hold positive charge and have enough potential to neutralize negative charge present on the dissolved and suspended species in water. During neutralization, the particles present in the aqueous system bind together or coagulate, giving rise to a process called "flocculation". The high weight flocs or bigger particles promptly settle down at the bottom of water over mechanism of settling called "sedimentation". Usually, during a conventional coagulation-flocculation process, efficient results are obtained to any type of wastewater in which dissolved and suspended particles are present. Direct flocculation is used in the treatment of organic effluents carrying suspended particles. In coagulation-flocculation process, cationic coagulant usually binds itself with non-ionic or anionic flocculent, whereas flocculants carrying anionic and cationic charges are selected for the process of direct flocculation. Numerous coagulants and flocculants (having variable charge density and molar weight) are utilized in wastewater treatment systems available on commercial grade. Flocculants having higher molecular weight are usually employed due to its linkage with bridging process that is strong relative to available flocculation mechanisms.

4.3. Flocculation Mechanism

There are several steps leading to floc formation such as: (i) dispersion of flocculent in solution system (ii) diffusion of flocculent to the solid and liquid interface (iii) adsorption of flocculent on surface of particles (iv) collision between particles carrying adsorbed flocculants as compared to other particles (v) leading to microflocs production (vi) adsorption of flocculent occurs on the particles due to successive collision and increase in size of microflocs to produce strong microflocs [2]. Numerous flocculation mechanisms have been proposed in order to explain the suspensions by polymers, colloidal destabilization and mechanism of floc formation e.g. polymer adsorption, displacement flocculation, neutralization (such as electrostatic patch effects), charge and depletion flocculation and polymer bridging etc. [8]. Principle flocculation processes for removing dissolved and suspended impurities in effluent water are explained as charge neutralization, electrostatic patch and bridge formation. These processes are dependent upon flocculent which are adsorbed on the surface of particles [8].

4.3.1. Charge Neutralization Mechanism

When adsorption sites and flocculent on particles are oppositely charged, the mechanism of charge neutralization is indicated as leading mechanism. However, cationic polyelectrolytes and inorganic flocculants such as metal salts and negatively charged hydrophobic colloidal particles are beneficial in wastewater treatment. The process of flocculation takes place due to less surface charge of particles i.e. zeta potential reduction and therefore reduced electrical repulsive forces between particles. This leads to van der waals forces of attraction to stimulate primary accumulation of colloids and conversion of suspended particles into microfloc. It was reported in many studies, that optimum flocculation takes place when polyelectrolytes dosages just enough to neutralize the charge of particles or to produce zeta potential close to zero, also known as its "isoelectric point" [8-24-27-29-33-35-43-46-53-64]. The colloidal suspensions existing in wastewater undergo destabilization and clusters are formed under influence of van der waals forces of attractions [65]. Charge reversal takes place if extra polymer is used and particles will be dispersed again, but with a positive charge instead of negative charge. The flocs obtained due to charge neutralization are fragile, loosely bound and settle down with passage of time. It is important to bind microflocs by adding high molecular weight polymers and using the effect of bridging, to achieve rapid sedimentation and high water recovery [64].

4.3.2. Chitosan as Charge Neutralization and Bridging Mechanisms

Chitosan has two basic functions in wastewater treatment (i) flocculation by bridging process (ii) coagulation by charge neutralization method [24]. Different types of mechanisms are used to explain the colloids destabilization and polymer suspensions for example polymer adsorption, polymer bridging, depletion flocculation, displacement flocculation and charge neutralization (comprising electrostatic patch effect) etc. [8-24-55]. When macromolecules having high charge density adsorb to substances, produce areas with positive and negative charges on the particle surface which results in patch flocculation. It causes strong electrical attraction between particles. Larger flocs having strong aggregation are formed. Due to adsorption of long chain polymers onto the surface of particles, polymer bridging takes place. When the adsorption sites and the polymers are of opposite charges, charge neutralization takes place. The mechanism of coagulation-flocculation engaged in elimination of dissolved and particulate pollutants using chitosan are precipitative coagulation, charge neutralization, adsorption (such as protonated amine groups), electrostatic patch and bridge formation (high molecular weight of bio-macro-molecules) as depicted in Fig 2.

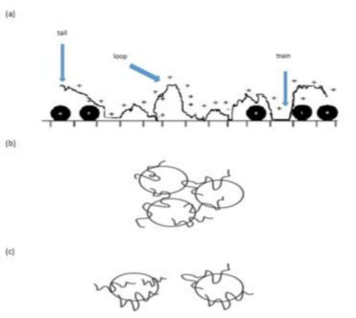

Figure 2: (a) Adsorption of polymers and formation of loop available for binding (b) Polymer bridging between particles (aggregation) and (c) Restabilization of colloides particles (floc breakups)

During the process of coagulation, colloidal contaminants are destabilized using charge neutralization and smaller particles merge to form large aggregates resulting in bridge formation. In coagulation, adsorption of dissolved organic substances onto the aggregates takes place, which can then be eliminated by sedimentation and filtration easily. Therefore, as compared to shorter chain polymers, longer chain polymers are more effective in nature. The process of flocculation occurs as a consequence of patch flocculation, charge neutralization and polymer bridging. The characteristic properties of chitosan such as charge density, molecular structure and molecular weight are very important for flocculation. The mechanism involved depends on various factors including pH, ionic strength and coagulant concentration of the solution [29]. The major distinctions between metal salts and cationic polymers are predominantly concerned with the degree of hydrolysis. Aluminium sulphate hydrolysis takes place simultaneously on contact with water giving rise to adsorption reactions. Whereas chitosan do not undergo hydrolysis at any given reaction conditions [29].

4.4. Electrostatic Patch

Electrostatic patch mechanism takes place when polyelectrolytes of less molecular mass and high charge density adsorb on surface of low density charge sites, hence reducing the capability of bridging. When highly cationic charge polymers adsorb on weak negative charge surface, to achieve neutrality overall, it is physically impossible for cationic polymer segment to neutralize each charged surface [66]. It leads to formation of cationic patches between uncoated areas of negatively charged surfaces. Close approach is one of the most important "patch wise" adsorption of particles. During the process, an electrostatic force of attraction between negative and positive patches is accountable for the process of flocculation and particle attachment [8]. Flocs formed are not as strong in contrast to those formed during bridging mechanism. Nonetheless, these flocs are stronger as compared to the flocs produced due to charge neutralization or a metal salt. Therefore, for effective electrostatic patch, high charge density of polyelectrolytes during flocculation is required. When charge density is lowered, bridging flocculation is favored [67].

4.5. Mechanism for Grafted Flocculants/Grafted Copolymers

Both polymer bridging and charge neutralization are involved in treatment of wastewater as grafted flocculants in the mechanism of flocculation [45-68-70]. Charge neutralization is dominant and generates number of insoluble complexes at a very high speed during initial phase of flocculation. Bridging effect is used to amass the insoluble complexes due to the flexible polymeric graft chains and construct extensive net structures like flocs. As a consequence, formation of compact flocs takes place and these rapidly settled down at the bottom [70-71]. Recent research studies reported that bridging is most crucial step of flocculation process [45-48]. Graft copolymers are preferred over the linear polymers for flocculation process due to polymer bridging mechanism. Bridge formation takes place between the neighboring particles and finally all they are linked together by the adsorption of polymeric chain segments onto the particles surfaces. Adsorbed polymer molecules are inclined to get an extended configuration, in order to interact with numerous particles because the polymer chains of grafted flocculants are lengthier. In other words, the radius of gyration is higher as shown in Fig 3.

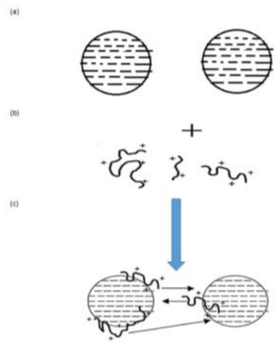

Figure 3: (a) Negatively charged particles (b) Cationic flocculants (c) Charge neutralization flocculation by patch mechanism while Arrows in (c) Attraction of opposite charges

Table 1: Principal properties of chitosan in relation to its use in water and waste treatment applications [72-74]

Principal Characteristics	Potential Applications
Non-toxic	Flocculent to clarify water (drinking, water, pools)
Biodegradable	Reduction of turbidity in food processing effluents
Renewable resource	Flocculation of bacterial suspensions
Ecologically acceptable polymer (environmental friendly)	Interactions with negatively charged molecules.
Efficient against bacteria, viruses and fungi	Recovery of valuable products (proteins)
Formation of salts with organic and inorganic acids	Chelation of metal ions
Ability to form hydrogen bonds intermolecularly	Removal of dye molecules by adsorption process
Ability to encapsulate	Polymer assisted ultrafiltration
Removal of pollutants with outstanding pollutant-binding capacities	Sludge treatment
	Filtration and separation

Table 2: Examples of effluents treated by coagulation/flocculation using chitosan

Effluent	Reference(s)
Food, seafood and fish processing wastes	[75-76]
Wastewater from milk processing plant	[77]
Brewery wastewater	[75-76]
Surimi wash water	[78-79]
Inorganic suspensions	[27-80]
Bacterial suspensions	[80-81]
Effluents containing humic substances	[82-83]
Effluents containing dyes	[29-84]
Pulp and paper mill wastewater	[85-86]
Olive oil wastewater	[87-89]
Oil-in-water emulsions	[87]
Aquaculture wastewater	[89]
Effluent containing metal ions	[90-91]
Effluent containing phenol derivatives	[92]
Partially purified sewage	[93]
Brackish water	[94]
Raw drinking water	[95]

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