Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.812993

52 (2014) 6030–6039
September

Taylor & Francis
Taylor & Francis Group

Effectiveness of natural coagulants from non-plant-based sources for water and wastewater treatment—a review

Packiam Saranya, Srikrishnaperumal Thanga Ramesh*, Rajan Gandhimathi

Department of Civil Engineering, National Institute of Technology, Tiruchirappalli, Tamilnadu, India
Tel. +91 431 2503166; Fax: +91 431 2500133; email: stramesh@nitt.edu

Received 19 April 2013; Accepted 1 June 2013

ABSTRACT

The natural polymers used in water and wastewater treatment systems include starches, galactomannans, cellulose derivatives, chitosan, microbial polysaccharides, gelatin, glues, and alginate. These natural coagulants are capable of treating water from high to low turbid water and having removal efficiency of sometimes more than 98% that can be used for drinking purposes. Naturally occurring coagulants are usually presumed safe for human health, while there is a fear that using aluminum salts may induce Alzheimer's disease. These natural coagulants are usually used as coagulant aid in combination with some synthetic coagulants, their effectiveness as the primary coagulant is still in beginnings. The mechanisms of treatment in these coagulants include intermolecular bridging, complexation process, adsorption, and charge neutralization. A review of non-plant-based natural coagulants, coagulating mechanisms, effectiveness, and its applications has been presented.

Keywords: Non-plant-based; Chitosan; Alginate; Turbid water; Coagulation

1. Introduction

The removal of suspended matter from water is one of the major goals of water treatment. Only disinfection is used more often or considered more important. In fact, effective clarification is really necessary for completely reliable disinfection because microorganisms are shielded by particles in the water. Clarification usually involves: coagulation, flocculation, settling, and filtration [1]. Flocculation–coagulation process plays a major role in surface water treatment by reducing turbidity, bacteria, algae, color, organic compounds, and clay particles [2]. The processes greatly increase the effectiveness of the latter processes by reducing or eliminating suspended particles that would otherwise clog filters or impair disinfection, thereby dramatically minimizing the risk of waterborne diseases [3,4]. Flocculating agents are generally divided into three groups: (1) inorganic flocculants, such as aluminum sulfate (AS), polyaluminum chloride, ferric chloride, and polyferric sulfate; (2) organic synthetic flocculants, such as polyacrylamide derivatives and polyethyleneimine; and (3) naturally occurring flocculants, such as chitosan, sodium alginate (SA) and bioflocculant [5]. There is growing interest in using ecologically friendly and biodegradable flocculants for wastewater treatment, which are advantageous because they are natural, renewable, non-toxic, and biodegradable. Materials commonly used as "green" flocculants combine typical flocculants such as aluminum or ferric chloride with

*Corresponding author.

synthetic polymers or new eco-sustainable materials such as inorganic salts or chitosan, organosepiolite particles, and different oily materials, such as palm oil and surfactants [6]. Over the recent years, the use of natural polymeric materials has been tested in water treatment to establish the value of the available biological resources and elimination of the possible negative impact of the synthetic polymers on human health, due to the presence of residual monomers from manufacturing process and reaction byproducts. Some natural polymers, such as polysaccharides, have been suggested to be moderately efficient due to their low molecular weights and high shear stability and they were noted to be cheap and easily available from reproducible farm and forest resources. Additional advantages of these natural polyelectrolytes include safety for human health and a wider effective dose range of flocculations for various colloidal suspensions. Hence, natural organic polymers have been studied for their flocculating ability to replace inorganic coagulants in recent years [7].

The mechanisms associated with different natural coagulants are varied as well. It is imperative for relevant stakeholders to fully comprehend the technicalities involved when considering the coagulants for rural, domestic, or industrial water treatment. Works on the plant-based coagulant like Moringa oliefera are well ahead and exploration of coagulants extracted from non-plant-based coagulants is still at the level of infancy. To tackle this, this paper provides a review of the natural coagulants obtained from non-plant-based sources and mechanisms involved so that its usage can replace the chemical coagulants.

2. Non-plant-based coagulants—their sources, structure, and coagulating mechanisms

Polymeric coagulants can be cationic, anionic, or non-ionic, in which the former two are collectively termed as polyelectrolytes. Although the polymers used in water treatment are synthetic, natural polyelectrolytes are pervasive. Many studies concerning natural coagulants referred to them as 'polyelectrolytes' even though many of these studies did not actually conduct in-depth chemical characterization to determine their ionic activity. As such, this term should be used carefully and be applied only after ionic activity is determined to be present in the coagulant. Natural coagulants are mostly either polysaccharides or proteins. In many cases, even though polymers labeled as non-ionic are not necessarily absent of charged interactions, there may be interactions between the polymer and a solvent within a solution environment as the polymer may contain partially charged groups including –OH along its chain [8].

2.1. Chitosan

Chitin is a cellulose-like biopolymer widely distributed in nature, especially in marine invertebrates, insects, fungi, and yeasts. Chitosan is the deacetylated derivative of chitin, a natural polysaccharide found primarily in the exoskeletons of arthropods and some fungi [8]. Chitosan is a biodegradable, non-toxic, linear cationic polymer of high molecular weight. Moreover, chitin extraction also does not cause any disturbance to the ecosystem, it embraces all advantages provided by polysaccharides, considering it as the source of chitosan [9]. Chitosan is a natural polysaccharide with many useful features such as hydrophilicity, biocompatibility, and the capability of adsorbing a number of metal ions because of its amino groups [10].

2.1.1. Chemical structure

The primary unit in the chitin polymer is 2-deoxy-2-(acetylamino) glucose. These units are combined by 1-4 glycosidic linkages forming a long chain linear polymer [11]. It is a linear polysaccharide comprising copolymers of glucosamine and N-acetyl glucosamine linked by (1–4) glycosidic bonds. The molar fraction of glucosamine residues is referred to as the degree of deacetylation [9,10].

Fig. 1 shows the chemical structure of chitosan. The chitosan can also complex with oppositely charged polymers such as polyacrylic acid, sodium salt of polyacrylic acid, carboxymethylcellulose, xanthan, carrageenan, alginate, pectin, heparin, hyaluronan, sulfated cellulose, dextran sulfate, and chondroitin sulfate [13,14].

2.1.2. Coagulating mechanism

The high content of amine groups in chitosan provides cationic charge at acidic pH and can destabilize colloidal suspension to promote the growth of large, rapid-settling floc that can then flocculate [15].

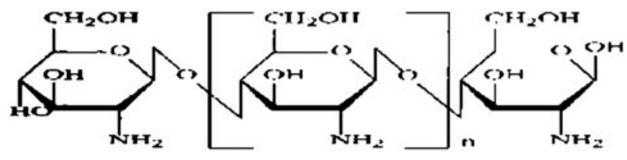

Fig. 1. Chemical structure of chitosan [12].

Because it is a long–chain polymer with positive charges at natural water pH, it can effectively coagulate natural particulate and colloidal materials, which are negatively charged, through adsorption, charge neutralization, inter-particle bridging, as well as hydrophobic flocculation [16,17].

2.1.3. Solubility

Chitosan is insoluble in water or in alkaline solutions at pH levels above about 6.5 or in organic solvents. It is soluble in acidic solution, which makes it more available for application. It dissolves readily in dilute solutions of most organic acids, including formic, acetic, tartaric, and citric acids. Chitosan is soluble to a limited extent in dilute inorganic acids except, phosphoric and sulfuric acids [11,18,19]. In order to dilute the chitosan powder for the preparation of chitosan stock solution, it has to be dissolved in acetic acid solution or hydrochloric acid solution and has to be continuously agitated for several hours [20].

In its crystalline form, chitosan is normally insoluble in an aqueous solution above pH 7; however, in diluted acids (pH 6.0), the protonated free amino groups on glucosamine facilitate solubility of the molecule [9]. Chitosan has a low solubility at a physiological pH of 7.4 or higher pH as it is a weak base with pKa values ranging from 6.2 to 7. Adjusting the solution's pH to approximately 7.5 induces flocculation due to deprotonation and insolubility of the polymer [12].

2.2. Alginate

Alginates are quite abundant in nature, as they occur both as structural component in marine brown algae (phaeophyceae), comprising upto 40% of dry matter, and as capsular polysaccharides in soil bacteria. The industrial applications of alginates are linked to their ability to retain water and their gelling, viscosifying, and stabilizing properties. Alginic acid is the only polysaccharide, which naturally contains carboxyl groups in each constituent residue, and possesses various abilities for functional materials [21].

2.2.1. Chemical structure

The chemical structure of alginate is shown in Fig. 2. Alginate could be regarded as a true block copolymer composed of homopolymeric regions of M and G, termed M block and G blocks, respectively, interspersed with regions of alternating structure. Smidsrod et al. (1973) found that alginates have no regular repeating unit and that the distribution of the monomers along the polymer chain could not be described by Bernoullian statistics [22]. Knowledge of the monomeric composition is hence not sufficient to determine the sequential structure of alginates. Haug et al. (1966) 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 C2 (carbon in second position) and/or C3 (carbon in third position) in the bacterial alginates [23].

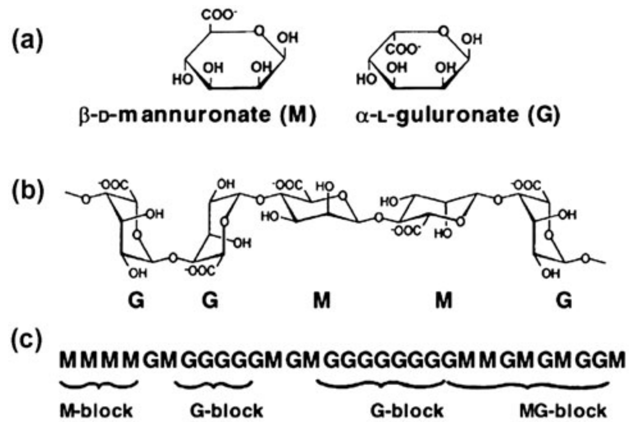

Fig. 2. (a) Alginate monomers, (b) Chain conformation, and (c) Block distribution [24,25].

Swelling of alginate gels can be increased dramatically by covalent cross-linking of performed Ca-alginate gels with epichlorohydrin followed by subsequent removal of Ca^{2+} ions by ethylene diamine tetra acetic acid. For the swelling behavior of dry alginate powder in aqueous media with different concentrations of Ca^{2+}, there seems to be a limit at approximately 3 mM free calcium ions [25].

2.2.2. Coagulating mechanism

The most useful and unique property of alginates is their ability to react with polyvalent metal cations, especially calcium ions to produce strong gels or insoluble polymers [26,27]. Alginate forms the so-called "egg-box" structure with calcium ions. The egg-box model of alginate is shown in Fig. 3. This gel formation property of alginate as well as other specific reactions with metal cations make alginate an industrially important biopolymer with wide applications [8]. The action of alginate is believed to be by one of the following mechanisms: charge neutralization along with bridging the gap between the particles or by the

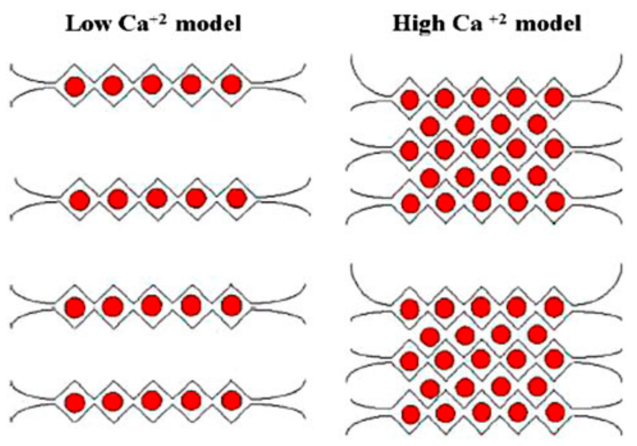

Fig. 3. Egg-box model of Alginate with high and low Ca^{2+} concentrations [29].

formation of calcium alginate gel, which is especially more effective at high calcium concentrations [28]. Calcium alginate gel combines with particles and captures them at the stage of gel formation or after gel formation. Finally, floc formed by the gel and the particle gets heavy enough and settles down [29].

2.2.3. Solubility

There are three essential parameters determining and limiting the solubility of alginates in water. The pH of the solvent is important, because it will determine the presence of electrostatic charges on the uronic acid residues. The total ionic strength of the solute also plays an important role and, obviously, the content of gelling ions in the solvent limits the solubility. In the latter case, the "hardness" of the water (i.e. the content of Ca^{2+} ions) is most likely to be the main problem [23,30]. Potentiometric titration revealed that the dissociation constants for the mannuronic and guluronic acid monomers were 3.38 and 3.65, respectively. The pKa value of the alginate polymer differs only slightly from that of the monomeric residues. An abrupt decrease in pH below the pK_a value causes precipitation of alginic acid molecules, whereas a slow and controlled release of protons may result in the formation of an "alginic acid gel." Alginate can be solubilized at (Ca^{2+}) above 3 mM by the addition of complexing agents, such as polyphosphates or citrate, before the addition of the alginate powder [31–33].

3. Applications

In water and wastewater treatment applications, chitosan has been used to synthesize membrane, used as an absorbent as well as a primary coagulant or flocculent [11]. Cationic chitosan forms polyelectrolyte complexes with polyanionic polymers and chelate complexes with metal ions to afford precipitates. These reactions have been used for the clarification of polluted waste water. Chitosan is also usable as an adsorbent for the removal of certain harmful radioisotopes from polluted water and for the recovery of uranium from sea water and fresh water [34]. Table 1 comprises all the principal properties of chitosan. SA has been used for the treatment of dye wastewater, humic acid, biosorption of heavy metals, etc. The advantages of alginate in various other fields are given in Table 2. The advantages of using these polymeric coagulants include that the sludge produced from polymeric coagulants dewater more readily than the sludge produced from metal salt coagulants.

Table 1
Principal properties of chitosan in relation to its use in water and wastewater treatment application [36]

Principal characteristics	Potential applications
Non-toxic	Flocculant to clarify water (drinking water, pools)
Biodegradable	Reduction of turbidity in food processing effluents
Renewable resource	Coagulation of suspended solids, mineral, and organic suspensions
Ecologically acceptable polymer (eliminating synthetic polymers, environment friendly)	Flocculation of bacterial Suspensions
Efficient against bacteria, viruses, and fungi	Interactions with negatively charged molecules, Sludge treatment
Formation of salts with organic and inorganic acids	Recovery of valuable products (proteins)
Ability to form hydrogen bonds inter-molecularly	Chelation of metal ions, filtration, and separation
Ability to encapsulate	Removal of dye molecules by adsorption processes
Removal of pollutants with outstanding pollutant-binding capacities	Reduction of odor, Polymer assisted ultrafiltration

Table 2
Applications of alginate in other fields

Food industry	• Stabilizer • Thickener and emulsion • Coacervation • Hydration
Pharmaceutical industry	• Dental impression material • Hemostatic • Preventing and exclusion from radioactive harmful metals • Salve, tablet, drugs
Printing and textile industry	• Printing agent • Synthetic fiber

Another advantage of polymeric coagulants is that they do not affect the pH of the effluent. Therefore, the pH does not have to be adjusted several times during the treatment process as is often required with the metal salt coagulants. This saves money and time in treating the water. The treatment of water with polymeric coagulants costs less overall than that treated with alum, comparing the sludge volume to be handled, the amount of polymer to be used, etc. [35]. Polymeric coagulants offer a broad range of applications, such as biocompatibility, biodegradation, biological activity, non-toxicity, non-allergenic, and ability for fiber and film formation [11].

3.1. Treatment of wastewater

Many natural coagulants may be inappropriate for the treatment of industrial wastewater due to their low availability for large-scale treatment and the extreme conditions (pH and concentration) of the wastewater, but usage of natural polymeric coagulants may afford benefits that can somewhat offset their disadvantages. Other than the evident sustainable and environmentally friendly aspects, natural polymeric coagulants also form stronger flocs via bridging effect with higher resistance to shear forces in a turbulent flow compared to non-polymeric coagulants such as alum [37,38]. Many methods have been described in the literature for color removal from wastewater containing dye. These include adsorption (e.g. on active carbon), coagulation–flocculation, chemical oxidation (chlorination, ozonization, etc.), and photodegradation (UV/H_2O_2, UV/TiO_2, etc.) [39–42]. As these dyes are also toxic for microorganisms, they often inhibit bacterial growth [43–46]. Consequently, conventional biological treatments cannot be directly applied to textile wastewater and a preliminary decolorization step based on physicochemical treatments is compulsory before biochemical oxygen demand (BOD_5) abatement [47–50].

The ability of chitosan in adsorbing metal ions could be improved by several modifications on chitosan such as cross-linking, controlled N-acylation and N-alkylation with several functional groups. Chitosan is recognized as excellent metal ligands, forming complexes with many metal ions, thus enhancing the removal of toxic metal from industrial wastewater. Besides the reactive primary and secondary hydroxyl groups, chitosan's versatility as an adsorbent is a function of its highly reactive amino group at the second carbon (C2) position [51]. The protonation of the chitosan amino groups (NH2) in solution makes the chitosan positively charged (exhibited as cationic polyelectrolytes) and thereby, very attractive for flocculation and different kinds of binding applications, by allowing the molecule to bind to a negatively charged surface via ionic or hydrogen bonding [52]. It has been shown to effectively remove metals such as boron [52], molybdenum, arsenic, gold, cadmium, vanadium, chromium, lead, cobalt, iron, manganese, silver, copper, nickel, mercury, and zinc from aqueous solutions [53]. In addition, it has been proved that chitosan could coagulate and flocculate a variety of suspensions or wastewater including mash and lauter wastewater of brewery [54], fish-meal factories [55], mineral colloids [56], river silt [57], latex particles [58], microorganisms [59], and palm oil mill effluent [60]. Table 3 summarizes the recent works on chitosan for the treatment of waste water.

3.2. Alginate as coagulant aid

For the application in industrial wastewater treatment, the study of the effect of alginate is still at the level of infancy. Not much works have been studied in this regard and alginate is being used with other primary coagulants by some researchers. Table 4 shows the work done so far and the efficiency of the coagulant as coagulant aid. The effect of coagulant aid SA on the coagulation behavior and floc characteristics of AS was investigated by Caihong et al. (2012) for synthetic dye wastewater treatment. They found that color removal was more enhanced by SA at low alum doses than at higher ones. Besides, they also ascertained that the combined action of AS–SA significantly improved the floc recoverability as reflected by higher recovery factors, compared to AS. Zhao et al. in 2012 studied the coagulation performance of dual coagulants alum, ferric chloride, and titanium tetra chloride with SA. They investigated the coagulation performance of dual coagulants in terms of turbidity

Table 3
Recent studies on chitosan for the treatment of waste water

Acid used for dissolving coagulant	Pollutant type	Optimum parameter values	Maximum removal efficiency (%)	Reference
Acetic acid	Algae	Neutral pH; dosage = 5–20 mg/L depending on algal species	Turbidity removal = 90%	[61]
0.1 N HCl	Textile waste water	Dosage = 30 mg/L; pH = 4	COD Reduction = 72.5%; Turbidity reduction = 94.9%	[62]
HCl	Boron	Dosage = 0.8 g/L; pH = 5	TSS = 94.2%; Turbidity = 91%; Boron = 79.7%	[8]
0.1 M HCl	Palm oil mill effluent	Dosage = 400 mg/L; pH = 6	Turbidty = 99.90%; TSS = 99.15%; COD = 60.73%	[63]
2 M HCl	Olive mill waste water	Dosage = 400 mg/L; pH = 4.5	TSS = 81%	[64]

Table 4
Recent works on Alginate as coagulant aid

Primary coagulant	Pollutant type	Optimum parameter value	Max. removal efficiency	Reference
Aluminum sulfate, Ferric chloride, Titanium tetra chloride	Humic acid	SA = 1 mg/L; Alum = 1.5 mg/L; $FeCl_3$ = 6 mg/L; $TiCl_4$ = 6 mg/L	Floc recoverability = 74%; DOC Removal = 62%;	[5]
Aluminum sulfate	Dying waste water	Aluminum sulfate = 6.5 mg/L; Alginate = 1.0 mg/L	Color removal = 86%	[65]

reduction and dissolved organic carbon removal and the flocs were characterized in terms of size, growth rate, strength, recoverability, and structure. The results showed that dual coagulants could remove HA effectively with appropriate SA doses. Primary coagulants plus SA exhibited an apparent improvement in both floc growth rate and floc size. Besides, floc recoverability was significantly increased. It was suspected that SA addition may have a positive effect on the solid–liquid separation process. However, dual coagulants gave the flocs with more open structure.

3.3. Treatment of turbid water

All natural coagulants exhibit highly effectual turbidity removal capabilities, some of them removing up to 99% of initial turbidity. Such efficiencies are certainly comparable to the established chemical coagulants (e.g. alum) [7]. Kaolin and clayey particles are predominantly negatively charged [66] with a zeta potential of approximately −9.40 mV [6].

Chitosan has no considerable potential to be used in the treatment of hard water, especially in medium and high turbidities. It was also found that chitosan did not affect the alkalinity. The addition of chitosan contributes to total organic carbon increase in the solution that could affect the coagulation mechanism [67]. But, Bina et al. (2009) verified that chitosan could be used as natural coagulant aid for drinking water treatment with the lowest risks of organic release.

In the process of alginate coagulation, the dosing order plays a very important role. The function of calcium in coagulation is due to its ability to compress the double layer and to reduce repulsive forces between colloid/colloid, polymer/colloid, and polymer/polymer pairs. Since both the surface and the polymer were negatively charged, adding calcium first eased up the approach of alginate to the particles. Additionally, calcium ion can form complexes with certain ionogenic groups on the polymer and on the particle surfaces. Even though the calcium alginate gel formation is believed to be the main mechanism, it is also thought that the gel combines with the particles and captures them at the stage of gel formation or after the gel formation. Finally, the floc formed by the gel and the particle gets heavy enough to settle down. Due to this, the higher the particle concentration (high turbidity), the better is the effectiveness of the system.

Table 5
Recent works done on the treatment of water using non-plant-based coagulants

Coagulant	Acid used for dissolving coagulant	Optimum parameter value	Max. removal efficiency	Reference
Chitosan	0.1 M HCl solution	pH = 7.0−7.5	Turbidity removal (kaolin) = 74.3–98.2%	[66]
Chitosan	1% Acetic acid	Dosage = 5 mg/L; chitosan conditioned by $NaHSO_4$	Turbidity removal (bentonite): Conditioned chitosan = 83.9% Unconditioned chitosan = 72.8%	[68]
Alginate	–	Alginate dosage = 0.001–10 mg/L; $CaCl_2$ dosage = 30–200 mg/L depending on turbidity.	Turbidity removal (smectite) = 98%	[6]
Chitosan	0.1 M HCl	Optimum pH = 8.1; Optimum dosage = 18 mg/L	Turbidity removal efficiency (sea water) = 97.5%	[69]
Chitosan and Aluminum sulfate	1% HCl	Chitosan dosage = less than 5 mg/L; Al dosage = 13.5 mg/L	Residual turbidity below 10 NTU; Sludge volume ratio = 30–40 mL/L	[70]

At very low doses of alginate and moderate calcium concentrations, calcium alginate is able to produce turbidity levels satisfying drinking water quality [6]. Rey et al. (2012) found that calcium alginate worked independent of alkalinity and performance depended on the presence of high concentrations of calcium in the system, but higher the calcium concentration, higher the amount of sludge produced. Table 5 shows the recent works done on the treatment of water using non-plant-based coagulants.

4. Cost of non-plant-based natural coagulants

Cost is an important parameter when choosing the processes and the substances to be used in environmental engineering. For all the systems where decisions are to be made for different processes, a cost-benefit analysis should be done. These analyses reveal which process and what substances are more feasible for that particular system [30]. In terms of commercialization, the bottom line is that it will always be based primarily on whether the scale-up system can sustain similar treatment performance at comparable (or reduced) cost with the natural coagulants when compared with established chemical coagulants. There are a few anecdotal reports that provide the costs of raw materials of the coagulants but direct comparisons in terms of coagulant types, processing stages, and prices in different geographical regions are a very complicated task given the different exchange rates, inflation factor, and varying accuracies of the costing values [7]. A coagulant that performs over a large range of pH levels will eliminate the need for pH correction. This in turn reduces costs by minimizing the need for additional materials and testing [71]. Despite the lack of evidence regarding the health effects of residual aluminum, there is an obvious advantage in developing biodegradable coagulants such as chitosan where cost and performance are comparable [72].

Bixler and Porse (2010) report the unit price of a commercial grade alginate used in industrial applications to be \$12/kg. The food grade calcium chloride is approximately \$1/kg. The unit price of industrial grade chitosan is approximately \$19/kg. On the other hand, the bulk price of alum is approximately \$0.3–0.5/kg (the latter two prices were obtained from the bulk suppliers in Turkey). In the case of alum coagulation, the pH adjustment and alkalinity addition may also be necessary that brings some extra cost [56]. One observation of the study made by Bixler and Porse is, even though the price of alginate is high, it is used in much smaller quantities compared to calcium that is used in this work and alum at its typically used doses during water treatment. With the prices given above and assuming that 80 mg/L of calcium and 0.2 mg/L of alginate are used and alternatively 3 mg/L Al(III) of alum is used to treat the same water, it is calculated that coagulation with calcium alginate would cost about eight times higher compared to alum [73]. In this calculation, chemical cost typically required for pH adjustment during alum coagulation was not taken into account. Even though it looks expensive, it is believed that it could be possible to reduce the cost of calcium alginate coagulation by increasing the effectiveness of the system using alginate of better and more suited quality for the work to be done [73].

Table 6
Unit prices of chemicals [30]

Chemical	Unit price (YTL/kg)	Amount required (g/m^3)	Total price (YTL/m^3)
Alum sulfate	0.37	0.03	11.1×10^{-3}
Polyelectrolyte	2.00	1×10^{-4}	2×10^{-4}
Calcium chloride	0.72	0.12	8.64×10^{-2}
Alginate	2.61	4×10^{-4}	10.44×10^{-4}

Table 7
Total chemical cost [30]

Total cost of alum–polyelectrolyte system	11.3×10^{-3} YTL/m^3
Total cost of calcium–alginate system	87.44×10^{-3} YTL/m^3

In order to compare the cost of chemicals between alum–polyelectrolyte system and calcium–alginate system usage, the alum, polyelectrolyte, calcium and alginate concentrations are selected as 30, 0.05, 120, and 0.4 mg/L, respectively. The values for alum and polyelectrolyte are the concentrations being used in IWTP for all initial turbidity values in the range of 5–100 NTU. Whereas, the concentration values of calcium and alginate are determined as a result of the 80 NTU of initial turbidity experiment, which is considered as the most efficient case [30]. Table 6 gives the unit prices of these chemicals. The prices stated in Table 6 are taken from the firms Türk Henkel and Interlab, Turkey. Table 7 summarizes the total chemical costs of both systems to meet the desired residual turbidity.

As it can be seen that chemical cost of both of the systems are comparable, this proves that calcium–alginate system can be used as an alternative coagulant. Moreover, it should be stated that these cost values are calculated by considering only the chemical costs and not operational costs and costs associated with further treatment of sludge originating from coagulation–flocculation process. Although operational costs of both of the systems are close to each other, the cost of sludge handling is expected to create huge differences. Because, it is known in general that the sludge originating from alum–polyelectrolyte system is in much higher quantities, it is very difficult to be treated. However, the calcium–alginate sludge is expected to be in much smaller quantities which can be handled easier to decrease the treatment cost [30].

5. Availability

The usage of these natural coagulants is currently restricted to small-scale projects and academic research, for the reason that the knowledge about harvesting of these coagulants were not familiar in the past decades. Chitosan, itself, is not a product that occurs in nature but it can be biodegraded within two months in farming soils in the summer [74]. Recently, the major production of alginate is carried out in Asia-Pacific, Europe, and Americas. Therefore it is possible that alginate can be produced in large quantities. Many industrial applications rely on this worldwide production. The world market of alginate production reached to about 30,000 tons in 2009 which showed about 25% expansion compared to the production in 1999 [33]. Therefore, it seems that these coagulants are available for industrial applications including water treatment.

6. Conclusion

In recent days, more researches are being done on the natural coagulants due to the detrimental nature of the synthetic coagulants. Natural coagulants are eco-friendly and does not cause any harm to the consumers. Plant-based coagulants are also advantageous, but in some cases it does not serve the purpose due to its organic nature. Knowledge on the extraction techniques of these materials is not adequate and is confined to some particular areas. So, the researchers should shell out their attempts to realize the true value of these non-plant eco-friendly materials that can be made use of in all applications of water treatment.

References

[1] L. Ravina, N. Moramarco, Everything you want to know about coagulation & Flocculation, Zeta-Meter, Staunton, 1993.
[2] N.E. Nwaiwu, A.A. Bello, Effect of Moringa oleifera-alum ratios on surface water treatment in North East Nigeria, Res. J. Appl. Sci. Eng. Technol. 3 (2011) 505–512.
[3] L.D. Mackenzie, D.A. Cornwell, Introduction to Environmental Engineering, 2nd ed., McGraw Hill, New York, 1991, pp. 160–161.
[4] O. Fatoki, A. Ogunfowokan, Effect of coagulant treatment on the metal composition of raw water, Water Res. 28 (2002) 293–298.
[5] Y.X. Zhao, Y. Wang, B.Y. Gao, H.K. Shon, J.H. Kim, Q.Y. Yue, Coagulation performance evaluation of sodium alginate used as coagulant aid with aluminum sulfate, iron chloride and titanium tetrachloride, Desalination 299 (2012) 79–88.
[6] R.D. Rey, H.A. Devrimci, A.M. Yuksel, F.D. Sanin, Algal alginate: A potential coagulant for drinking water treatment, Desalination 299 (2012) 16–21.
[7] C.Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, J. Process Biochem. 45 (2010) 1437–1444.

[8] M.A. Abu-Hasan, L.S. Hui, Z.Z. Noor, Removal of Boron from Industrial wastewater by chitosan via chemical precipitation, J. Chem. Nat. Resour. Eng. 4 (2009) 1–11.
[9] A. Montembault, C. Viton, A. Domard, Physico-chemical studies of the gelation of chitosan in a hydroalcoholic medium, J. Biomater. Appl. 26 (2005) 933–943.
[10] Y. Inukai, Y. Tanaka, T. Matsuda, N. Mihara, K. Yamada, N. Nambu, O. Itoh, T. Doi, Y. Kaida, S. Yasuda, Removal of boron (III) by N-methylglucamine type cellulose derivatives with higher adsorption rate, Anal. Chim. Acta 511 (2004) 261–265.
[11] Q.P. Peniston, E. Johnson, Process for the Manufacture of Chitosan. US Patent No. 41951755, 1980.
[12] T.W. Wong, Chitosan and its use in design of insulin delivery system, Recent Pat. Drug Deliv. Formul. 3 (2009) 8–25.
[13] R. Hejazi, M. Amiji, Chitosan-based gastrointestinal delivery systems, J. Controlled Release 89 (2003) 151–165.
[14] M.M. Issa, M. Köping-Höggård, P. Artursson, Chitosan and the mucosal delivery of biotechnology drugs, Drug Discovery Today 2 (2005) 1–6.
[15] J. Roussy, M. Van Vooren, B. Dempsey, E. Guibal, Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions, Water Res. 39 (2005) 3247–3258.
[16] N.M. Alves, J.F. Mano, Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications, Int. J. Biol. Macromol. 43 (2008) 401–414.
[17] Q. Li, L. Kegley, Assessing the effectiveness and environmental impacts of using natural flocculants to manage turbidity, Oregon Department of Transportation Research Unit, Oregon, OR, 2005.
[18] J.G. LeHoux, F. Grondin, Some effects of chitosan on liver function in the rat, Endocrinology 132 (1993) 1078–1084.
[19] Sigma-Aldrich (1999), Search Results for: 9012-76-4. Available fromhttps://www.sigma-aldrich.com
[20] J.R. Pan, C.P. Huang, S.C. Chen, Y.C. Chung, Evaluation of a Modified chitosan Biopolymer for Coagulation of Colloidal Particles, Colloids Surf. A 147 (1999) 359–364.
[21] A. Ikeda, A. Takemura, H. Ono, Preparation of low-molecular weight alginic acid by acid hydrolysis, J. Carbohydr. Polym. 42 (2000) 421–425.
[22] O. Smidsrod, R.M. Glover, S.G. Whittington, The relative extension of alginates having different chemical composition, J. Carbohydr. Res. 27 (1973) 107–118.
[23] A. Haug, B. Larsen, A Study on the composition of alginic acid by partial acid hydrolysis, Proc. Int. SeaWeed Symp. 5 (1966) 271–277.
[24] E. Atkins, D.T. Mackey, W. Smolko, Crystalline structures of alginic acids, Nature 225 (1970) 626–628.
[25] F.G. Fischer, H. Dorfel, The Polymerisation of Brown algae (carbohydrate of Algae), J. Physiol. Chem. 302 (2012) 186–203.
[26] K.I. Draget, O. Smidsrod, G. Skjak-Break, Alginates from algae, Polysaccharides and Polyamides in the food industry, Properties, Products and Patents, John Wiley, Weinheim, 2005, pp. 1–30. ISBN: 3-527:31345-1
[27] A.H. King, Brown seaweed extracts (alginates), in: M. Glicksman (Ed.), Food Hydrocolloids, 2 (1983) 115–188.
[28] G.T. Grant, E.R. Morris, D.A. Rees, P.J.C. Smith, D. Thom, Biological interactions between polysaccharides and divalent cations: The egg-box model, FEBS Lett. 32 (1973) 195–198.
[29] N.E. Simpson, C.L. Stabler, C.P. Simpson, A. Sambanis, I. Constantinidis, The role of the $CaCl_2$–guluronic acid interaction on alginate encapsulated βTC3 cells, J. Biomater. 25 (2004) 2603–2610.
[30] H.A. Coruh, Use of Calcium Alginate as coagulant in Water, Middle East Technical University: M.S. thesis, 2005.
[31] A. Haug, B. Larsen, O. Smidsrod, A Study on the composition of alginic acid by partial acid hydrolysis, J. Acta Chem. Scand. 20 (1966) 183–190.
[32] A. Haug, B. Larsen, O. Smidsrod, Studies on the sequence of uronic acid residues in alginic acid, J. Acta Chem. Scand. 21 (1967a) 691–704.
[33] A. Haug, O. Smidsrod, Precipitation of polysaccharides by salts in ethanol-water-mixtures, J. Polym. Sci. 16 (1967) 1587–1598.
[34] S. Hirano, Chitin biotechnology applications, J. Biotechnol. Annu. Rev. 2 (1996) 237–258.
[35] D.J. Nozaic, S.D. Freese, P. Thompson, Longterm experience in the use of polymeric coagulants at umgeni water, J. Water Sci. Technol. 1 (2001) 43–50.
[36] F. Renault, B. Sancey, P.M. Badot, G. Crini, Chitosan for coagulation/flocculation processes—An eco-friendly approach, Eur. Polym. 45 (2009) 1337–1348.
[37] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (2007) 2301–2324.
[38] R.W. Peters, T.J. Walker, J.E. Eriksen, T.K. Cheng, Y. Ku, W.M. Lee, Wastewater treatment—physical and chemical methods, J. Water Pollut. Control Fed. 57 (1985) 503–517.
[39] M.V.B. Zanoni, J. Sene, M.A. Anderson, Photoelectrocatalytic degradation of Remazol Brilliant Orange 3R on titanium dioxide thin-film electrodes, J. Photochem. Photobiol. A 157 (2003) 55–63.
[40] B. Zielinska, J. Grzechuslka, A.W. Morawski, Photocatalytic decomposition of textile dyes on TiO_2-Tytanpol A11 and TiO_2-Degussa P25, J. Photochem. Photobiol. A 157 (2003) 65–70.
[41] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw, Water Res. 36 (2002) 2824–2830.
[42] M. Perez, F. Torrades, X. Domenech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents, Water Res. 36 (2002) 2703–2710.
[43] B. Neppolian, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar/UV induced photocatalytic degradation of three commercial textile dyes, J. Hazard. Mater. 89 (2002) 303–317.
[44] A. Pala, E. Tokat, Color removal from cotton textile industry wastewater in an activated sludge system with various additives, Water Res. 36 (2002) 2920–2925.
[45] Y.M. Slokar, A.M. Le Marechal, Methods of decoloration of textile wastewater, Dyes Pigm. 37 (1998) 335–356.
[46] S.F. Kang, H.M. Chang, Coagulation of textile secondary effluents with Fenton's reagent, J. Water Res. 36 (1997) 215–222.
[47] W. Chu, S.M. Tsui, Modeling of photo decoloration of azo dye in a cocktail photolysis system, Water Res. 36 (2002) 3350–3358.
[48] J.H. Churchly, Removal of dye waste color from sewage effluent—the use of full scale ozone plant, J. Water Sci. Technol. 30 (1994) 275–284.
[49] A.J. Greaves, D.A.S. Phillips, J.A. Taylor, Correlation between the bio elimination of anionic dyes by an activated sewage sludge with molecular structure, Dyes Pigm. 1 (1999) 363–365.
[50] A. Alinsafi, M. Da Motta, S. Le Bonté, M.N. Pons, A. Benhammou, Effect of variability on the treatment of textile dyeing wastewater by activated sludge, Dyes Pigm. 69 (2006) 31–39.
[51] V.D. Savant, J.A. Torres, Chitosan-based coagulating agents for treatment of cheddar cheese whey, J. Biotechnol. Progr. 16 (2000) 1091–1097.
[52] D.A.S. Gamage, The used of chitosan for the Removal of Metal Ions Contaminants and Proteins from Water, Memorial University of Newfoundland: Msc. thesis, 2003.
[53] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, Kinetics of cadmium uptake by chitosan-based crab shells, Water Res. 36 (2002) 3219–3226.
[54] W.P. Cheng, F.H. Chi, R.F. Yu, Y.C. Lee, Using chitosan as a coagulant in recovery of organic matters from the mash and lauter wastewater of brewery, J. Polym. Environ. 13 (2005) 383–388.
[55] L. Guerrero, F. Omil, R. Mendez, J.M. Lema, Protein recovery during the overall treatment of wastewater from fish-meal factories, J. Bioresour. Technol. 63 (1998) 221–229.
[56] C. Huang, Y. Chen, Coagulation of colloidal particles in water by chitosan, J. Chem. Technol. Biotechnol. 66 (1996) 227–232.

[57] R. Divakaran, V.N.S. Pillai, Flocculation of river silt using chitosan, Water Res. 36 (2002) 2414–2418.
[58] M. Ashmore, J. Hearn, Flocculation of model latex particles by chitosans of varying degrees of acetylation, Langmuir 16 (2000) 4906–4911.
[59] S.P. Strand, K.M. Vårum, K. Østgaard, Interactions between chitosans and bacterial suspensions: Adsorption and flocculation, Colloids Surf. B 27 (2003) 71–81.
[60] A. Ariffin, R.S.A. Shatat, A.R. Nik Norulaini, A.K. Mohd Omar, Synthetic polyelectrolytes of varying charge densities but similar molar mass based on acrylamide and their applications on palm oil mill effluent treatment, Desalination 173 (2005) 201–208.
[61] J.Q. Jiang, J.D. Graham, Enhanced coagulation using Al/Fe (III) coagulants: Effect of coagulant chemistry on the removal of color-causing NOM, J. Environ. Technol. 17 (1996) 937–950.
[62] M.A. Abu-Hasan, M.H. Puteh, Pretreatment of Palm oil mill effluent (POME): A Comparison study using chitosan and alum, MJCE 19 (2007) 128–141.
[63] M.A. Abu-Hasan, T.P. Li, Z.Z. Noor, Coagulation and flocculation treatment of waste water in textile industry using chitosan, J. Chem. Nat. Resour. Eng. 4 (2009) 43–53.
[64] L. Rizzo, G. Lofrano, M. Grassi, V. Belgiorno, Pre-treatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes, Sep. Purif. Technol. 63 (2008) 648–653.
[65] C. Wu, Y. Wang, B. Gao, Y. Zhao, Q. Yue, Coagulation performance and floc characteristics of aluminum sulfate using sodium alginate as coagulant aid for synthetic dying wastewater treatment, Sep. Purif. Technol. 95 (2012) 180–187.
[66] A. Ndabigengesere, K.S. Narasiah, Quality of water treated by coagulation using Moringa oleifera seeds, Water Res. 32 (1998) 781–791.
[67] B. Bina, M.H. Mehdinejad, M. Nikaeen, H. Movahedian Attar, Effectiveness of chitosan as natural coagulant aid in treating turbid water, Iran. J. Environ. Health Sci. Eng. 6 (2009) 247–252.
[68] T. Chatterjee, S. Chatterjee, S.H. Woo, Enhanced Coagulation of bentonite particles in water by a modified chitosan polymer, J. Chem. Eng. 148 (2009) 414–419.
[69] H. Altaher, The use of chitosan as a coagulant in the pretreatment of turbid sea water, J. Hazard. Mater. 233 (2012) 97–102.
[70] C.Y. Hu, S.L. Lu, C.L. Chang, F.L. Chen, Y.D. Wu, J.L. Ma, Treatment of highly turbid water using chitosan and aluminum sulphate salts, Sep. Purif. Technol. 104 (2013) 322–326.
[71] K. Kurita, Chitin and chitosan: Funtional biopolymers from marine crustaceans, J. Mar. Biotechnol. 8 (2006) 203–226.
[72] L. Rizzo, A. Di Gennaro, M. Gallo, V. Belgiorno, Coagulation/chlorination of surface water: A comparison between chitosan and metal salts, Sep. Purif. Technol. 62 (2008) 79–85.
[73] H.J. Bixler, H. Porse, A decade of change in seaweed hydrocolloids industry, J. Appl. Phycol. 23 (2010) 321–335.
[74] C. Huang, S. Chen, J.R. Pan, Optimal condition for modification of chitosan: A biopolymer for coagulation of colloidal particles, Water Res. 34 (2000) 1057–1062.