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Review

Emerging usage of plant-based coagulants for water and wastewater treatment

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ABSTRACT

A review of plant-based coagulant sources, processes, effectiveness and relevant coagulating mechanisms for treatment of water and wastewater is presented. These coagulants are, in general, used as point-of-use technology in less-developed communities since they are relatively cost-effective compared to chemical coagulants, can be easily processed in usable form and biodegradable. These natural coagulants, when used for treatment of waters with low-to-medium turbidity range (50–500 NTU), are comparable to their chemical counterparts in terms of treatment efficiency. Their application for industrial wastewater treatment is still at their infancy, though they are technically promising as coagulant for dyeing effluent as afforded by Yoshida intermolecular interactions. These natural coagulants function by means of adsorption mechanism followed by charge neutralization or polymeric bridging effect. Frequently studied plant-based coagulants include nirmali seeds (*Strychnos potatorum*), *Moringa oleifera*, tannin and cactus. Utilization of these coagulants represents important progress in sustainable environmental technology as they are renewable resources and their application is directly related to the improvement of quality of life for underdeveloped communities.

Contents

1. Introduction

Highly industrialized and fast developing countries rely substantially on large-scale industrialization to boost their global economic competitiveness. Concurrently, tremendous economic growth which is spurred by robust manufacturing industries has also generated significant quantities of organic, inorganic and metal contaminants. As a direct result, the influx of these anthropogenic-based contaminants into the earth's surface environment, particularly the surface water environment, has increased substantially over the past century. The implications of these contaminants in terms of public, ecological and environmental health, have been well documented. These detrimental effects are, unfortunately, more apparent and observable in developing countries due to their less stringent environmental regulations and difficulty in constructing, operating and maintaining proper water or wastewater treatment systems due to high fixed costs, especially in the case of rural areas [1].

Due to the lack of proper water treatment systems in these rural or underdeveloped communities, the best immediate option is to use simple and relatively cost-effective point-of-use (POU) technologies such as coagulation [2]. Coagulation is an essential process in the treatment of both surface water and industrial wastewater. Its application includes removal of dissolved chemi-

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cal species and turbidity from water via addition of conventional chemical-based coagulants, namely, alum ($AlCl_3$), ferric chloride ($FeCl_3$) and polyaluminium chloride (PAC). While the effectiveness of these chemicals as coagulants is well-recognized [3,4], there are, nonetheless, disadvantages associated with usage of these coagulants such as ineffectiveness in low-temperature water [5], relatively high procurement costs, detrimental effects on human health, production of large sludge volumes and the fact that they significantly affect pH of treated water. There is also strong evidence linking aluminium-based coagulants to the development of Alzheimer's disease in human beings [6]. It is therefore desirable to replace these chemical coagulants with plant-based coagulants to counteract the aforementioned drawbacks.

The main advantages of using natural plant-based coagulants as POU water treatment material are apparent; they are cost-effective, unlikely to produce treated water with extreme pH and highly biodegradable. These advantages are especially augmented if the plant from which the coagulant is extracted is indigenous to a rural community. In the age of climate change, depletion of earth's natural resources and widespread environmental degradation, application of these coagulants is a vital effort in line with the global sustainable development initiatives. Usage of plant-based coagulants for turbid water treatment dates back to over several millennia ago [7] and thus far, environmental scientists have been able to identify several plant types for this purpose. While it is understandable that the coagulants are meant as simple domestic POU technology, there have also been numerous studies focused on their usage for treatment of industrial wastewaters. 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 either rural, domestic or industrial water treatment. To address this, this paper provides an overview of the natural coagulant sources, processes and mechanisms involved so that environmental specialists can tailor its usage for a myriad of water contaminants.

To provide a more focused discussion, natural coagulants derived from non-plant sources such as chitosan (widely produced from exoskeleton of crustaceans) [8] and isinglass (produced from fish swim bladders) [9,10] are excluded from this review. This exclusion is based on practicability, since non-plant sources are less likely to have the potential for mass production compared to plant sources. It is surprising to note that a comprehensive critical analysis of available plant-based coagulants is still non-existent given the importance of sustainable environmental technology in the 21st century and hopefully this review can provide an immediate platform for environmental scientists to intensify their research on these natural materials.

2. Natural plant-based coagulants and coagulation mechanisms

Polymeric coagulants can be either cationic, anionic or non-ionic, in which the former two are collectively termed as polyelectrolytes [11]. 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, as 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.

It is imperative to fully grasp the underlying coagulation mechanisms associated with these natural coagulants so that complete understanding of their usage can be realized. Aggregation of particulates in a solution can occur via four classic coagulation mechanisms: (a) double layer compression; (b) sweep flocculation; (c) adsorption and charge neutralization; and (d) adsorption and interparticle bridging [2,11–13]. The presence of salts [or suitable coagulants] can cause compression of the double layer [14] which destabilizes the particulates. Sweep flocculation occurs when a coagulant encapsulates suspended particulates in a soft colloidal floc. Adsorption and charge neutralization refer to the sorption of two particulates with oppositely charged ions while interparticle bridging occurs when a coagulant provides a polymeric chain which sorbs particulates [2]. Polymeric coagulants are generally associated with mechanisms (c) and (d) as their long-chained structures (especially polymers with high molecular weights) greatly increase the number of unoccupied adsorption sites. It appears that these two mechanisms provide underlying principles to the inner workings of plant-based coagulants as well and they are the focus of discussion in the following sections. The existence of background electrolytes in aqueous medium can facilitate the coagulating effect of polymeric coagulants since there is lesser electrostatic repulsion between particles. Although many plant-based coagulants have been reported, only four types are generally well-known within the scientific community, namely, nirmali seeds (*Strychnos potatorum*), *Moringa oleifera*, tannin and cactus.

2.1. Nirmali seeds

S. potatorum (nirmali) is a moderate-sized tree found in Southern and central parts of India, Sri Lanka and Burma, used predominantly as a traditional medicinal extract [15]. Sanskrit writings from India reported that the seeds were used to clarify turbid surface water over 4000 years ago [16,17] which indicated that they were the first reported plant-based coagulant used for water treatment. Most studies concerning its use as coagulant seem to be limited within the Indian subcontinent [16,18–20].

Nirmali seed extracts are anionic polyelectrolytes that destabilize particles in water by means of interparticle bridging [21]. Previous studies [16,21] have established that the seed extracts also contain lipids, carbohydrates and alkaloids containing the –COOH and free –OH surface groups which enhance the extracts' coagulation capability. Adinolfi et al. [22] report that a mixture of polysaccharide fraction extracted from *S. potatorum* seeds contained galactomannan and galactan capable of reducing up to 80% turbidity of kaolin solution. In all cases, the galactomannans are made up of a main chain of 1,4-linked β-D-mannopyranosyl residues bearing terminal α-D-galactopyranosyl units linked at the 0–6 position of some mannose residues [23]. Although the specific coagulation mechanism associated with nirmali seed extracts has not been extensively investigated, one can surmise that the presence of copious amount of –OH groups along chains of galactomannan and galactan provides weakly but abundant adsorption sites that ultimately lead to the aforesaid coagulant interparticle bridging effect. Since both ionic ($–COO^-H^+$) and comparatively non-ionic (galactomannan) groups or substances are suggested to be present in the extract, the author deems that its designation as 'anionic polyelectrolytes' is premature, as there are no identified studies that provide detailed elucidation of its coagulation mechanisms and percentage composition of the extract. As such, further studies are required in this aspect.

2.2. M. oleifera

M. oleifera (horseradish or drumstick tree), a non-toxic (at low concentrations) tropical plant found throughout India, Asia, sub-

Saharan Africa and Latin America [7,24] whose seeds contain an edible oil and water soluble substance [25], is arguably the most studied natural coagulant within the environmental scientific community. It is widely acknowledged as a plant with numerous uses with almost every part of its plant system can be utilized for beneficial purposes. *Moringa* is most frequently used as food and medicinal sources within less-developed communities. A succinct summary of its various uses afforded by its different plant parts such as leaves, flowers, seeds, roots and bark is provided by Anwar and Bhanger [26]. It has been reported that rural communities in African countries utilize its crude seed extracts to clear turbid river water. Muller [27] and Jahn [24,28] were among the earliest researchers to study the use of *M. oleifera* as natural coagulant. Since then, there has been several studies [29–31] conducted to optimize its usage as low-cost POU water treatment technology, with emphasis on application within the African continent. However, research on natural coagulants in the 80s and early 90s was still scarce as information on their efficacies had been limited to anecdotal reports and few academic journal articles.

The seminal paper by Ndabigengesere et al. [25] published in year 1995 is the first literature that comprehensively elucidates the basic coagulation mechanisms inherent in *M. oleifera* as applied for turbid water treatment and it essentially sparked widespread interests among environmental scientific community from then onwards. It is suggested that its active coagulating agents are dimeric cationic proteins with molecular mass of 12–14 kDa and isoelectric point (p*I*) between 10 and 11 and its main coagulation mechanism is adsorption and charge neutralization. Since then, however, there have been conflicting reports on the exact nature of the active coagulating agent present in *Moringa*. Gassenschmidt et al. [32] reports that the coagulating agent is a protein with a molecular mass of 6.5 kDa and p*I* greater than 10 while Ghebremichael et al. [33] suggests that it is a cationic protein with p*I* greater than 9.6 and molecular mass less than 6.5 kDa. Conversely, Okuda et al. [34] argue that the active component from an aqueous salt extraction is not a protein, polysaccharide or lipid, but an organic polyelectrolyte with molecular weight of approximately 3.0 kDa. Although most research groups seem to agree that the active agent is cationic protein, the findings by Okuda et al. [34] should not be disregarded as there could be a myriad of unidentified coagulating agents in *Moringa*, albeit the degree of their coagulating capability may be slighter compared to the cationic protein.

In many cases, impurity particles are negatively charged and cationic polyelectrolytes are the most efficient coagulants, which bodes well for usage of *Moringa* as coagulation agent. It is well-established that electrostatic interaction provides strong adsorption in these systems and that neutralization of the particle surface and even charge reversal can occur [11]. All these technical factors ultimately attract the interest of the scientific community to continue on research of using *Moringa* to treat a wide spectrum of turbid waters or even industrial wastewaters. Its coagulating capability can be further enhanced by addition of cations. In a study conducted by Okuda et al. [35], it is established that bivalent cations (e.g. Ca^{2+} and Mg^{2+}) significantly enhance the coagulating effect of *M. oleifera* extracts in which the cations may have adsorbed to the active components to form insoluble net-like structure to capture suspended kaolin particles.

2.3. Tannin

Tannin is a general name given to large polyphenol compounds obtained from natural materials, for example, the organic extract from bark and wood [36] of trees such as *Acacia*, *Castanea*, or *Schinopsis* [37]. It is a polymer with molecular weights ranging from hundreds to tens of thousands and traditionally used as a tanning agent in the leather industry. There have been conflicting reports

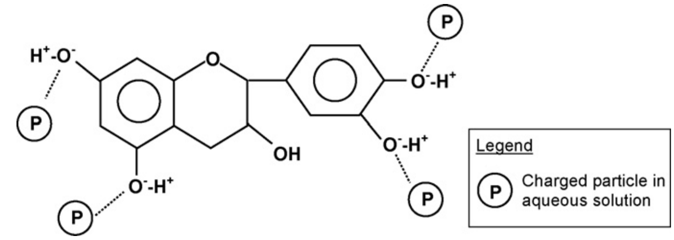

Fig. 1. Schematic representation of basic tannin structure in aqueous solution and possible molecular interactions.

on the effect of tannin on human health [38] and its portrayal in this negative light may have limited its application as natural coagulant for water treatment. Nonetheless, such application is still a preferred research area for many researchers. Özacar and Şengil [39–41] have been studying the application of tannin as either standalone coagulant or coagulant aid for water treatment. The tannin used in their study is extracted from valonia, which is obtained from the corn cup of the oak that grows in Asia Minor. They conclude that tannin is an excellent substitute to chemical coagulants.

The effectiveness of tannin as a natural coagulant for water treatment is influenced by the chemical structure of tannins that have been extracted from plant and degree of tannin modification [39]. The presence of phenolic groups in tannin clearly indicates its anionic nature since it is a good hydrogen donor. Fig. 1 illustrates the schematic representation of basic tannin structure in aqueous solution and possible molecular interactions that induce coagulation. It is common knowledge that phenolic groups can easily deprotonate to form phenoxide which is stabilized via resonance. This deprotonation is attributed to delocalization of electrons within the aromatic ring which increases the electron density of the oxygen atom. This provides an indication that the more phenolic groups are available in a tannin structure, the more effective its coagulation capability. An interesting study on application of a commercial tannin containing both amine and phenonic groups for water treatment conducted by Graham et al. [36] suggests that their 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 as a consequence of presence of phenolic groups.

2.4. Cactus

Application of cacti species for water treatment is rather recent compared to other natural coagulants such as nirmali or *M. oleifera*. The most commonly studied cactus genus for water treatment is *Opuntia* which is colloquially known as 'nopal' in Mexico or 'prickly pear' in North America. This cactus type has long been associated with its medicinal properties [42] and dietary food sources [43]. Besides *Opuntia*, other cactus species including Cactus latifaria [44] have also been successfully used as natural coagulants.

The high coagulation capability of *Opuntia* is most likely attributed to the presence of mucilage which is a viscous and complex carbohydrate stored in cactus inner and outer pads that has great water retention capacity [45]. Previous studies have established that mucilage in cactus *Opuntia* contains carbohydrates such as L-arabinose, D-galactose, L-rhamnose, D-xylose, and galacturonic acid [45,46]. Zimmerman and co-researchers [2] recently report that galacturonic acid is possibly the active ingredient that affords the coagulation capability of *Opuntia* spp. though it should be noted that it only accounts for only 50% of turbidity removal. Nonetheless, this is still a significant quantum and therefore, this compound deserves further evaluation on its contribution to the overall coagulation capability of cactus. They suggest that *Opun-*

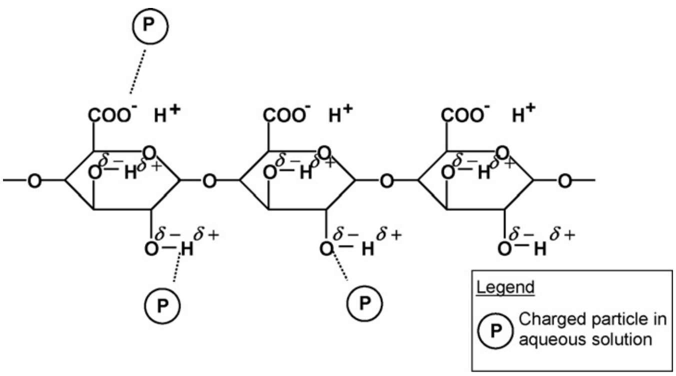

Fig. 2. Schematic representation of polygalacturonic acid in aqueous solution and possible dominant molecular interactions associated with adsorption and bridging.

tia spp. operates predominantly through a bridging-coagulation mechanism where solution particulates do not directly contact one another but are bound to a polymer-like material that originates from the cactus species. Interestingly, galacturonic acid was also reported by Japanese researchers in the late 90s to be present in natural microbial-based coagulants produced by *Enterobacter* sp. [47], *Pseudomonas* sp. [48] and *Klebsiella pneumoniae* [49]. All these studies point to the importance of galacturonic acid which possibly acts as one of the major active coagulating agents in plants and therefore, deserves further technical assessment.

Though not extensively reported in open literatures, it is highly possible that galacturonic acid [a major constituent of pectin in plants] exists predominantly in polymeric form [polygalacturonic acid] [50] that provides a 'bridge' for particles to adsorb on. Relevant dominant molecular interactions associated with adsorption and bridging in coagulation are shown in Fig. 2. The polygalacturonic acid structure evidently indicates that it is anionic due to partial deprotonation of carboxylic functional group in aqueous solution. The existence of such functional groups along the chain of polygalacturonic acid implies that chemisorption between charged particles and $-COO^-$ may occur although this requires further empirical substantiation. The presence of –OH groups along its polymeric chain also infers possible intramolecular interactions which may distort the relative linearity of the chain, though this is not extensively investigated by Zimmerman and co-researchers [2].

3. Processing steps

The general processing steps involved in production of plant-based coagulants can be divided into three major stages, namely, primary, secondary and tertiary (Fig. 3). The primary processing step is very straightforward and most research studies and domestic applications utilize only this processing step to simulate the traditional method of drying and subsequent pulverizing of plant parts into fine powder generally used by local communities in the absence of sophisticated processing equipment. Nonetheless, an obvious setback emerges since the prepared powder contains not just the coagulating active agents, but also plant tissues. The latter is rich in organic constituents and increases organic loadings in the treated water which may exacerbate the situation further, rather than improving the treatment efficiency [33]. This problem can be addressed by processing the powder through secondary (extraction) and tertiary (purification) stages. This works by extracting their active coagulating agents and subsequently purifying them to eliminate undesired organics. This may increase their processing costs and may not be practical as POU water treatment technology. Nonetheless, extraction of active coagulating agents is still a noteworthy aspect which may prove useful should they be commercialized or applied in concentrated form for industrial wastewater treatment.

In the secondary processing stage, extraction of the active agents can be performed via different solvents (organic, water or salt solution), which at first glance, are rather surprising as they are somewhat dissimilar given their distinct chemical structures and electrostatic properties. In most cases, different solvents are jointly used at this stage to extract useful and edible oil [33] and active coagulants in separate sub-steps. Extraction using water is evidently the most accepted choice due to its abundance and cost-effectiveness, especially for *M. oleifera* as its active coagulating agent is water-soluble protein. Nonetheless, extraction using salt solution (NaCl) has been reported by Okuda et al. [34,35,51] to be superior to water. They found that by using NaCl solution extraction, the extracted components showed better coagulation activity with dosages 7.4 times lower than components extracted by distilled water for the removal of kaolinite turbidity. They attributed this enhanced effect to the salting-in mechanism in proteins wherein a salt increases protein–protein dissociations and protein solubility as the salt ionic strength increases.

Tertiary processing is rarely done in the case of plant-based coagulants and is presently restricted to academic research on purification of *M. oleifera* extracts [25,33,34] since it apparently increases the overall processing cost. Preliminary studies suggest that lyophilization [25], ion-exchange [33] and dialysis [34] are feasible purification methods for *M. oleifera* extracts which can be incorporated into a scaled-up setup for treatment of higher throughput of turbid water. Such methods have not been extensively applied to other plant-based coagulants and this presents opportunities for other research.

4. Treatment of waters with low-to-medium range turbidity

Table 1 summarizes recent studies on natural coagulants for treatment of water with low-to-medium range turbidity. Such studies imply application of these coagulants as a simplistic POU technology meant for treatment of turbid surface waters with approximate values ranging from 50 to 500 NTU. All the natural coagulants exhibit highly effectual turbidity removal capabilities, with some of them removing up to 99% of initial turbidity. Such efficiencies are certainly comparable to the established chemical coagulants (e.g. alum). Optimum dosages are generally within the range from 10 to 60 mg/L. Natural coagulants are most effective at basic waters as evident by the optimum pH values from 7 to 10.

In the case of *M. oleifera,* the optimum pH is slightly basic [52] since at pH higher than 7, kaolin and clayey particles are predominantly negatively charged [25]. This enables adsorption to occur between kaolin particles and cationic polyelectrolytes from *Moringa* which destabilizes the former, rendering charge neutralization to occur. At pH lower than 7, the kaolin particles are less negatively charged which causes increased repulsion effect between the polyelectrolytes and particles. For cactus *Opuntia*, the effect of solution pH on coagulation is rather complicated and more difficult to elucidate due to the unclear nature of its coagulation agents, although it has been suggested that galacturonic acid (key component in mucilage of *opuntia*) plays a key role in coagulation of kaolin particles. Since galacturonic acid is essentially an anionic polyelectrolyte, the following reactions may occur in aqueous solution:

$$\text{R-COOH} \rightleftharpoons \text{R-COO}^- + \text{H}^+ \quad (1)$$

$$\text{R-COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{R-COOH} + \text{OH}^- \quad (2)$$

In this case, R- represents the galacturonic acid backbone structure. For reaction (1), the carboxyl group of the galacturonic acid

Table 1
Recent studies on natural coagulants for treatment of waters with low-to-medium range turbidity.

Coagulant	Plant part	General preparation procedure	Highest recorded turbidity removal (%)	Selected optimum parameter value(s)[a]	Suggested coagulation mechanism	References
Moringa oleifera	Seed	Extraction of active agent using water and subsequent purification	• Kaolin (>94%)	• Dosage = 50 mg/L	Adsorption and charge neutralization	[25]
	Seed	DPP, diluted with 0.5% [v/v] HCl	• Lake water + clay (>96%) • (Lake water + clay (>99%))[c]	• Dosage = 60 mg/L • (Dosage = 14 mg/L)[c] • pH 7.9	-na-	[52]
	Seed	DPP	• Surface water (>99%)	• Dosage = 200 mg/L	-na-	[53]
Cactus *opuntia*	-na-	DPP	• Kaolin (up to 94%) • Sewage water (84%) • (Sewage water (≈90%))[b] • Seawater (>99%)	• Dosage = 50 mg/L (kaolin); 60 mg/L (sewage); 60 mg/L (seawater) • (Dosage ≈60 mg/L (sewage))[b] • pH 10 (kaolin)	-na-	[54]
	Pad and inner skin	DPP	• Estuarine water (up to 98%) • River water (up to 70%)	• Dosage ≈13 mg/L	-na-	[55]
	Pad	DPP	• Kaolin (≈98%)	• Dosage = 5–55 mg/L depending on turbidity strength • pH 10	Mainly bridging-coagulation	[2]
Cactus *latifaria*	-na-	DPP	• Kaolin (>90%)	• Dosage ≈10 mg/L	-na-	[44]
Tannin	Extract from *Acasia mearnsii* bark	Obtained as a solid from supplier	• Kaolin (≈75%) • (Kaolin (≈90%)][c]	• Dosage = 14 mg/L • pH 9	Adsorption, charge neutralization and interparticle bridging	[36]
Strychnos potatorum (Nirmali)	Seed	DPP	• Surface water (>96%)	• Dosage = 1.5 mg/L	-na-	[53]
Prosopis juliflora (Mesquite bean)	Seed	DPP	• Kaolin (>83%)	• Dosage ≈20 mg/L	-na-	[44]
Fabaceae (Guar gum)	Seed	Ground and pulverized	• Shallow well water (≈96%)	• Dosage = 50 mg/L	-na-	[56]
Jathropa curcas	Seed	Ground and pulverized	• Shallow well water (≈92%)	• Dosage = 50 mg/L	-na-	[56]
Maize	-na-	DPP, diluted with 0.5% (v/v) HCl	• Lake water + clay (>93%) • (Lake water + clay (>99%))[c]	• Dosage = 60 mg/L • (Dosage = 14 mg/L)[3] • pH 7.4–7.9	-na-	[52]

'-na-' denotes unavailable data.
'DPP' denotes 'dried and pulverized into powder'.
[a] This optimum value corresponds to the highest contaminant removal % obtained for the concerned parameter in which other parameters are fixed.
[b] Value obtained using $AlCl_3 \cdot 6H_2O$ as coagulant for comparison.
[c] Value obtained using alum as coagulant for comparison.

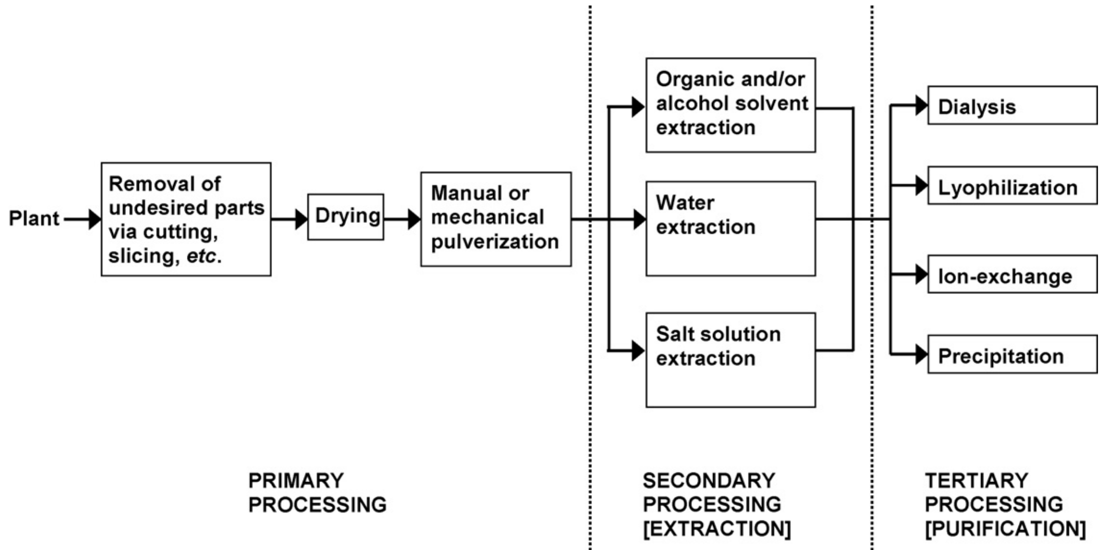

Fig. 3. General processing steps in preparation of plant-based coagulants.

partially dissociates affording the COO^- group which acts as a chemical adsorption site for cations (from kaolin and cactus extract [2] though the quantity of kaolin cations may be lesser at pH higher than 7). In the polymeric form of galacturonic acid, the quantity of available COO^- adsorption sites is affected by OH^- concentration in the solution as suggested by Eq. (2). At pH higher than 7, OH^- concentration increases and disrupts the equilibrium concentration of ions in the solution which subsequently shifts the equilibrium to the left and enables more protons to from the carboxyl group to form water molecules and exposes more COO^- adsorption sites. Admittedly, this may only represent one approach of elucidating the effect of pH on coagulation. Nonetheless, it can afford a preliminary understanding on the optimum coagulation conditions which is useful for further studies pertaining to manipulation of solution pH for enhancing effectiveness of natural coagulants.

5. Treatment of industrial wastewaters

Many natural coagulants may be inappropriate for treatment of industrial wastewaters due to their low availability for large-scale treatment and the extreme conditions (pH and concentration) of the wastewaters but usage of natural polymeric coagulants may afford benefits that can somewhat offset its disadvantages. Other than the evident sustainable and environmental-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 [11]. This implies that natural coagulants can be utilized within a batch stirred tank setup to treat contaminated industrial wastewaters, at least in a mechanical sense, since bridging linkages are more resistant to breakage at high shear levels. Muhle in 1985 [57] and 1987 [58] in particular, provided interesting empirical findings on the particle adhesion forces between polymers and particles and effects due to mechanical forces within batch stirred vessels. An underlying observation regarding these studies is that the stronger the flocs, the larger they can grow under given shear conditions.

So far, identified usage of natural coagulants for industrial wastewater has been limited to academic research. Many findings from these academic studies, however, indicate their good potential for industrial wastewater treatment. In many cases, the natural coagulants can perform at their best when used for treatment of wastewaters with less variety of contaminants. Early studies suggest that plant-based coagulants can be effectively used for treating selected dyeing effluent. Beltran-Heredia et al. [59] find that up to 80% Alizarin Violet 3R dye removal can easily achieved by using tannin-based coagulant. Blackburn [60] reports that galactomannan-containing plant gums (locust bean gum, guar gum, cassia gum) are capable of removing more than 70% of dyes (C.I. reactive red 238, C.I. direct black 22 and C.I. acid blue 193). Mishra and Bajpai [61] discover that mucilage of a food grade polysaccharide (*Plantago psyllium*) has the capability of removing up to 71% of C.I. Vat Yellow 4 dye while Sanghi et al. [62] report that seed guar gum is capable of removing up to 65% of Direct Orange dye. NaCl-extracted *M. oleifera* active coagulating compounds have been reported to achieve up to 99% Chicago Sky Blue 6B [63] and 80% Carmine Indigo dyes removal [64]. This research group also reports that *C. javahikai* seed gum is a good coagulant aid when used in conjunction with chemical coagulant for decolorization of dyes in varying ratios [65]. The mucilage of *P. psyllium* is reported to contain D-Xylose, L-arabinose and D-galacturonic acid with approximate analysis indicating 6.7–13.6% uronic acid and 78–91% pentosan [61]. This strongly implies that this mucilage functions predominantly through the adsorption-bridging mechanism which is similar to cactus mucilage. The high tendency of both ionic (*M. oleifera* and *P. psyllium* extracts) and relatively non-ionic (galactomannan) polysaccharides to adsorb dye molecules prior to bridging effect is most probably down to existence of unique intermolecular interaction between π-electron system from dye molecule and OH- group [electron-deficient hydrogen atom] from polysaccharide (Fig. 4) first suggested by Yoshida et al. [66] and later revisited by Blackburn and Burkinshaw [67]. This type of hydrogen bonding may contribute to substantive adsorption of dyes to highly solvated polysaccharides in aqueous solution due to the delocalized π-electron clouds of dye. This unique intermolecular interaction affords a technical justification for using natural coagulants to treat dyeing effluent, though other factors

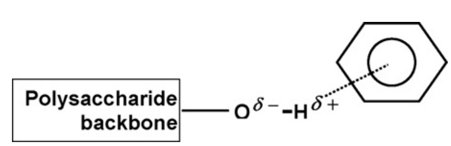

Fig. 4. Schematic representation of intermolecular interaction between π-electron from dye molecule and OH- group from polysaccharide (Yoshida H-bonding interaction).

such as bulk availability of natural coagulants and preference of wastewater treatment specialists to utilize established chemical coagulants may somewhat impede process development of the former.

Besides dyeing effluent, there are several studies conducted to evaluate the technical viability of using plant-based coagulants for other types of industrial wastewater, though their research aims are rather divergent. It appears that many of these coagulants are quite uncommon and represent new varieties of plant-based active coagulant extract besides the aforestated established plant coagulants. Among these varieties are Okra gum from seedpods of *Hibiscus esculentus* [68], Fenugreek mucilage (*Trigonella foenum-graecum*) [69], *Tamarindus indica* seed mucilage [70] and *Malva sylvestris* (mallow) mucilage [71]. These coagulants are used to treat tannery, sulphate/phosphate and biological-based wastewaters (wastewaters with high organic loading) with treatment efficiencies ranging from 40 to 95%. At this point, an inexperienced scientist may interpret such treatment efficiencies as high and thus directly imply that these extracts can replace established coagulants. Nonetheless, these results originate from the same research group and thus, may not be representative of the condition from a different geographical region. Hence, further studies should be conducted by other research groups to verify the veracity of such results. It should be noted that there is scarcity of comprehensive studies that compare the effectiveness of these natural coagulants with that of chemical coagulants and this may be one of the factors that inhibit their potential for industrial wastewater application.

6. Cost of plant-based coagulants

It has been espoused in previous sections that usage of plant-based coagulants provides environmental benefits and numerous lab-scale studies have proven that they are technically feasible for small-scale POU utilization. Nevertheless, 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. Thus, the costs stated here should be treated as an indication rather than absolute values.

A comprehensive survey conducted reveals that costing analysis of *M. oleifera* has been given priority over other natural coagulants and this is unsurprising given the well-publicized advantages of the plant. Sutherland et al. [72] assert that *Moringa* seed contains 40% by weight of oil and its presscake remain after oil extraction still contains the active coagulant. In the African country of Malawi, this presscake residue can be obtained at zero net cost as a by-product of oil extraction. In 1993, the purchase price of *Moringa* seed was MK 75 per 1000 m^3 water treated (MK 10.07 = £1 sterling in March 1993) compared to the cost of alum and soda ash which is MK 501 per 1000 m^3 water treated [72]. This implies the cost-effectiveness of using the natural coagulant as simple POU technology. However, such benefit is not noticeable in different countries, say Malaysia, where the cultivation cost for producing 1 kg (3400 seeds) of *M. oleifera* is approximately US $2 which is double the cost of alum at US $1 per kg [73] or in Botswana, where 1 kg seeds reportedly costs about US $27 [74]. Though the presented costing values are exclusively limited to *Moringa*, it can still be used to provide a baseline indication of the costing for other natural coagulants in general since the latter appear to be non-existent.

7. Conclusions

The usage of natural coagulants derived from plant-based sources represents a vital development in ‘grassroots’ sustainable environmental technology since it focuses on the improvement of quality of life for underdeveloped communities. Fortunately, it is surmised that usage of these coagulants is far more receptive by environmentalists worldwide since it avoids the common problem faced by biofuels usage where skeptics feel that their benefits are outweighed by global food shortage and deforestation caused by mass plantation of biofuel plants. Nonetheless, there are many pressing issues that are hindering process development of these coagulants, namely, absence of mass plantation of the plants that affords bulk processing, perceived low-volume market and virtually non-existent supportive regulation that stipulates the quality of the processed coagulant extracts [75]. The last factor is especially vital since it is normally difficult for regulatory authorities to endorse a product for sale to the general public. In view of this, it is felt that application is currently restricted to small-scale usage and academic research but it can benefit from fervent promotion and endorsement from relevant stakeholders, particularly the from the authorities. In technical terms, these natural coagulants are highly effectual for treatment of waters with low turbidity but may not be feasible in the case of wastewaters with extreme pH. As such, it is always prudent for water treatment practitioners to circumspectly select the most suitable natural coagulants and tailor them for specific proposes. Quite clearly, *M. oleifera* is the most researched plant-based coagulants but it is felt that further research can be conducted by using the information described in this review as a platform to discover other plant species which are non-toxic and can be mass produced. As a starting point, researchers should pay close attention to other plants with parts that have high active coagulation extract yields which contain recognized active coagulant agents including galacturonic acid.

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