APPLICATION OF PLANT BASED COAGULANTS FOR WASTE WATER TREATMENT

G. Vijayaraghavan*, T. Sivakumar*, A. Vimal Kumar**

Address for Correspondence
* Assistant Professor, Chemical Engineering, Adhiparasakthi Engineering College, Melmaruvathur
** Assistant Professor, Chemical Engineering, Arunai Engineering College, Thiruvannamalai

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.

KEYWORDS Natural coagulant, Plant based coagulant, Waste water treatment

1. INTRODUCTION
The production of drinking water from most raw water sources involves coagulant use at a coagulation/flocculation stage to remove turbidity in the form of suspended and colloidal material. Many coagulants and flocculants are widely used in conventional water treatment processes. These materials can be classified into inorganic coagulants (e.g. aluminium and ferric salts) and synthetic organic polymers (e.g. polyacryl amide derivatives and polyethylene imine). Aluminium salts are cheap and are the most widely used coagulants in water and wastewater treatment all over the world. Regarding the application of synthetic polymers, the presence of residual monomers is undesirable because of their neurotoxicity and strong carcinogenic properties. In recent years there has been considerable interest in the development of usage of natural coagulants which can be produced or extracted from microorganisms, animal or plant tissues. These coagulants should be biodegradable and are presumed to be safe for human health. In addition, natural coagulants produce readily biodegradable and less voluminous sludge that amounts only 20–30% that of alum treated counterpart [3]. The use of natural materials of plant origin to clarify turbid raw waters is not a new idea. Natural coagulants have been used for domestic household for centuries in traditional water treatment in tropical rural areas. Nowadays, some reports describe natural coagulants from Nirmali seed and maize mesquite bean and Cactus latifaria Cassia angustifolia seed and different leguminose species. Nevertheless, the material which has recently received the greatest degree of attention is the seed of Moringa oleifera indigenous to Sudan. The water extract of M. oleifera seeds compares quite favourably with aluminium salt.

2. COAGULATION
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. Coagulation is an essential process in the treatment of both surface water and industrial wastewater. Its application includes removal of dissolved chemical species and turbidity from water via addition of conventional chemical-based coagulants, namely, alum (AlCl₃), ferric chloride (FeCl₃) and polyaluminium chloride (PAC) [4]. While the effectiveness of these chemicals as coagulants is well-recognized, there are, nonetheless, disadvantages associated with usage of these coagulants such as ineffectiveness in low-temperature water, 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. It is therefore desirable to replace these chemical coagulants with plant-based coagulants to counteract the aforementioned drawbacks.

3. MERITS OF PLANT-BASED COAGULANTS
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 he 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 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 [1]. It is imperative for relevant stakeholders to fully comprehend the technicalities involved when considering the coagulants for 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) and isinglass (produced from fish swim bladders) 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 [10]. 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.

4. NATURAL PLANT-BASED COAGULANTS AND COAGULATION MECHANISMS

Polymeric coagulants can be cationic, anionic or nonionic, in which the former two are collectively termed as polyelectrolytes. 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 [2]. 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. The presence of salts [or suitable coagulants] can cause compression of the double layer 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. 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 [5]. 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.

4.1 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. Sanskrit writings from India reported that the seeds were used to clarify turbid surface water over 4000 years ago 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. Nirmali seed extracts are anionic polyelectrolytes that destabilize particles in water by means of interparticle bridging. Previous studies 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 [11]. 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 d-mannopyranosyl residues bearing terminal d-galactopyranosyl units linked at the 0–6 position of some mannose residues. 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 aforementioned 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.

4.2 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 whose seeds contain an edible oil and water soluble substance , 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. It has been reported that rural communities in African countries utilize its crude
Researchers have identified the coagulant component of treatment agents is growing nowadays. The investigation on these kinds of water treatment is necessary to purify the coagulant. However, the direct application of this isolated agent is not possible under the hypothesis of sustainable and appropriate technology. Consequently, the search for and simple and low cost purifications procedures as well as the use of the coagulant in combination with other coagulants and treatment processes needs to be adopted. Some examples of drinking water treatment using crude extract in pilot plant set up have been conducted.

4.3 Tannin
Tannin is a general name given to large polyphenol compounds obtained from natural materials, for example, the organic extract from bark and wood of trees such as Acacia, Castanea, or Schinopsis. 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 on the effect of tannin on human health and its portrayal in this negative light may have limited its application as natural coagulant 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. 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 suggests that their tannin is cationic in nature since there is a single tertiary amine group per monomer.

This tannin also exhibits amphoteric nature as a consequence of presence of phenolic groups.

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

4.4 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 and dietary food sources. Besides Opuntia, other cactus species including Cactus latifaria 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. Previous studies have established that mucilage in cactus Opuntia contains carbohydrates such as l-arabinose, d-galactose, l-rhamnose, d-xyllose, and galacturonic acid. Galacturonic acid is possibly the active ingredient that affords the coagulation capability of Opuntia spp. through it should be noted that it only accounts for only 50% of turbidity removal [9]. Nonetheless, this is still a significant quantum and therefore, this compound deserves further evaluation on its contribution to the overall coagulation capability of cactus. 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] 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 intra molecular interactions which may distort the relative linearity of the chain.
5. TREATMENT OF INDUSTRIAL WASTE WATERS
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 [7]. 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.

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. 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 [8]. 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. 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 explained 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 [3]. 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.

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 surprising 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. The cost-effectiveness of using the natural coagulant as simple POU technology. 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.

REFERENCES