Effectiveness of natural coagulants in water and wastewater treatment

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ABSTRACT
Natural waterways are contaminated due to industrialization, urbanization, population growth etc., degrading their quality. Contaminated waterways cause numerous health and environmental hazards. Therefore, it is imperative to remove contaminants. Coagulation is one of the efficient primary chemical treatment methods that could be used to treat such contaminants. Natural coagulants have gained popularity in the water and wastewater treatment industry due to their advantage over chemical coagulants. Natural coagulants are derived from either plants, animals, or microorganisms. This study has elaborated on the nature and mechanisms, and types of natural coagulants. In this review work, many studies have proposed several types of natural coagulants. However, plant-based natural coagulants extracted from different plant components have been extensively discussed and compared based on their application and efficiency in water and waste treatment. The primary purpose of this review is to refine the knowledge on the potential use and optimization of the effectiveness of eco-friendly and sustainable natural coagulants. Besides, the development efforts and the barriers reported by recent findings for the commercialization of natural coagulants are also discussed. Further, few modified natural coagulants have also been presented for exploring the other possible approaches to promote their usage in water and wastewater treatment in the future studies.
INTRODUCTION

Water is the fundamental requirement for all human activities and biological activities. It is the main component in the hydrological cycle. The water resources are continuously decreasing around the world due to various environmental degradation activities, climate change (Konapala et al., 2020), population growth (Zubaidi et al., 2020), and increasing standards of living and urbanization (Wu et al., 2013). Rapid population growth and haphazard waste disposal have resulted in the impending water crisis. In order to sustain the water requirements, various processes and technologies are being researched to improve the quality of water (Ullah et al., 2020). These technologies fall into three main categories, namely physical, chemical, and biological treatment methods. Physical methods include settling, media, and membrane filtration (Obotey Ezugbe and Rathilal, 2020), adsorption (Ali and Gupta, 2006), and UV processes (O’Malley et al., 2020). Coagulation (Alibeigi-Beni et al., 2021), disinfection (Collivignarelli et al., 2017), ion exchange (Ergunova et al., 2017), catalytic reduction (Guo et al., 2020; Sivakumar, 2015), oxidation (Gogate and Pandit, 2004), and softening processes (Brastad and He, 2013) are some of the chemical methods used in the wastewater treatment. Biological methods include microbial biodegradation (Huang et al., 2018), phyto remediation (Hu et al., 2020), bioreactor processes (Neoh et al., 2016), constructed wetlands (Wu et al., 2015) etc. Moreover, some processes are combined with others to improve efficiency (Ang and Mohammad, 2020). One of the most widely used processes in water and wastewater’s primary treatment is coagulation for removing suspended particulate matter and colloids in wastewater (Staicu et al., 2015). Coagulation is considered one of the simple methods to remove suspended solids and impurities in water efficiently. Successful coagulation can be attained by using either chemical-based (inorganic and synthetic organic) coagulants or natural coagulants (de Paula et al., 2018). Natural coagulants have been recognized for their traditional local water purification (Choy et al., 2014; Dorea, 2006). Naturally occurring coagulants are sustainable, environmentally friendly, and less toxic than chemical coagulants (Teh et al., 2014). Natural coagulants have grasped the scientific community’s attention in the past decades due to their significant health and environmental benefits, and it solves most of the common problems associated with chemical coagulants. Natural coagulants are produced or extracted from different sources such as microorganisms, animals, or plants (non-plant-based and plant-based). Now, several effective coagulants which have plant origin are being identified. Some of the common ones include Hibiscus sabdariffa (Roselle seeds) (Mohd-Esa et al., 2010), Dolichos lablab (Hyacinth bean) (Daverey et al., 2019), Moringa oleifera (Nonfodji et al., 2020), Nirmali seeds (Prabhakaran et al., 2020) watermelon seeds (Bhattacharjee et al., 2020) and cactus species (Rebah and Siddeeg, 2017). The drawbacks of chemical coagulants have resulted in the search for eco-friendly and sustainable natural coagulants in their usage and production. The main advantages of natural coagulants are renewability, biodegradability, nontoxicity, and cost-effectiveness. These studies have already proved the effectiveness of natural coagulants in wastewater treatment applications (Choy et al., 2014; Yin, 2010). However, the industrial usage of natural coagulants in wastewater treatment applications is limited. This is mainly due to the processing cost and the performance consistency of the extracted compounds from natural sources. Due to this, researchers tend to focus on modifying natural coagulants to get the maximum benefits (Muruganandam et al., 2017; Ahmed et al., 2016). This study aims to identify potential research gaps to refine the knowledge on natural coagulants and summarize the optimization methods for coagulants for improving their efficiency in water and wastewater treatment. This study also showcases the application of these coagulants for large-scale commercial usages and may assist in future studies. These will be discussed in sections as follows: the need for natural coagulants, mechanisms of natural coagulants, types of natural coagulants, barriers in the commercialization of natural coagulants, and examples of modified or blended natural coagulants. This study has been carried out in Colombo, Sri Lanka, in 2021.

Need for natural coagulants

Chemical coagulant used has raised controversial issues due to its toxic nature for living organisms and can be categorized into three types: hydrolyzing metallic salts, pre-hydrolyzing metallic salts, and synthetic cationic polymers (Freitas et al., 2018; Verma et al., 2012). Due to the low cost, easy handling, storage, and high availability, chemical coagulants are more prevalent in wastewater treatment processes.
Al$_2$(SO$_4$)$_3$· Fe$_2$(SO$_4$)$_3$, AlCl$_3$, and FeCl$_3$ are the most commonly used coagulant salts (Freitas et al., 2018; Matilainen et al., 2010; Sher et al., 2013). Despite the availability, low cost etc.; chemical coagulants are far behind in green chemistry due to high residual concentrations of aluminum found in treated wastewater (Freitas et al., 2018; Matilainen et al., 2010). According to Freitas et al., 2018; McLachlan 1995; Polizzi et al. 2002, Alzheimer’s disease is linked with the neurotoxicity of aluminum. Synthetic polymer coagulants form hazardous secondary products such as acrylamide which is carcinogenic and neurotoxic, and also synthetic polymers have low biodegradability (Freitas et al., 2018; Kurniawan et al., 2020). Excessive concentrations of chemical coagulants such as aluminum reduce the pH of water tends and also, they can be accumulated to food chains (Kurniawan et al., 2020). Improper disposal of toxic sludge pollutes the groundwater and soil. Accumulation of toxic sludge, such as aluminum, iron etc., in natural water bodies causes adverse effects on aquatic organisms and plant species (Kurniawan et al., 2020). Hence there is a need for the efficient utilization of natural coagulants for water and wastewater treatment.

Mechanism of coagulation by natural coagulants

Coagulation occurs between the coagulant added, the impurities, and the alkalinity of the water, resulting in the formation of insoluble flocs. Flocs are the agglomerations of particulate suspended matter in the raw water, reaction products of the added chemicals, colloidal and dissolved matter from the water adsorbed by these reaction products. Unprocessed water from the reservoir contains organic and inorganic impurities, such as silt, rotten substance, alga, bacterium, etc. Hence coagulation is the essential step in water purification. In addition, coagulants make suspensions in water to gather and reduce the turbidity of water (Z. Song et al., 2009). The successful coagulation of natural coagulants (Ang et al., 2020) stands on these three pillars: characteristics of coagulant used, characteristics of water to be treated, characteristics of mixing process (Ang et al., 2020; Kumar et al., 2017). As Fig. 1 shows, these coagulation factors play a significant role in determining the most efficient coagulant required for the treatment. Coagulants’ molecular weight (Ang et al., 2020; Gautam and Saini, 2020), types of equipment and reagents used, chemical and physical properties of the pollutants such as zeta potential (Ang et al., 2020), color, the concentration of the colloidal particles, the presence or absence of impurities (trace elements and dissolved salts (ions and chemicals) also affect the coagulation process (Ang et al., 2020; Kumar et al., 2017; Muruganandam et al., 2017). If the natural coagulant contain positive surface charge, its coagulation activity against negatively charged suspended particles will be higher and vice versa for negatively charged natural coagulants with positively charged suspended particles. Functional groups also contribute to surface charge (Ang et al., 2020). Molecular weight of natural coagulant is very important in particle bridging. If the molecular weight of natural coagulant is higher, it can form strong bridges with the particles and it leads to the formation of strong flocs and improve settling (Ang et al., 2020). Mixing is another critical step in the coagulation process. Fast mixing increases the interactions between coagulants and suspended particles and forms micro flocs. Slow mixing leads to the aggregation of micro flocs into large flocs (Kurniawan et al., 2020). Coagulation also affects the other steps of the treatment process. An efficient and effective coagulation process favors the microbiological quality (Kumar et al., 2017) of the end product and increases the lifetime of filters (Kumar et al., 2017), reducing the total cost of treated water.

Natural coagulants are composed of carbohydrates, protein, and lipids. The primary building blocks are the polymer of polysaccharides and amino acids. According to the previous research, the main mechanisms governing coagulation activity are charge neutralization and polymer bridging.
Polymer bridging is preceded by polymer adsorption. Because of the affinity between long-chain polymers and colloidal particles, long-chained polymers can attach to the colloidal particle’s surface. A part of the polymer is attached to the particle while the other parts form loops and tails. These loops and tails are the main structure of polymer bridging loops, and tails allow attaching to other colloidal particles and form larger flocs. The basis of charge neutralization is known as the electrostatic patch mechanism. The patches of positive and negative regions on the particle’s surface cause the additional attraction between particles. Ionizable polymer (polyelectrolytes) is used as a coagulant in the charge neutralization mechanism. It stabilizes the negatively charged colloidal particles. Polycation is used to stabilize the particles, gaining near to zero zeta potential. The optimum dosage of polyelectrolyte needed will be determined by the charge density of the polyelectrolyte (Amran et al., 2018; Yin, 2010). Natural coagulants have varied mechanisms of action. Let us consider some of the coagulation mechanisms of natural coagulants.

As shown in Table 1 Chitin is a cellulose-like biopolymer. It is found in fungi, marine invertebrates, yeasts, and insects. Chitosan is formed by the deacetylation of chitin (Hassan et al., 2009; Saranya et al., 2014). It is efficient in cold waters at low concentrations, producing less sludge and sludge degraded by microorganisms. Both charge neutralization (has positively charged amino group) and bridging are the two coagulation mechanisms identified. Chitosan is a potential substitute for metallic salts and synthetic polyelectrolytes used in wastewater treatment (Nechita, 2017). Chitosan has a high content of amino groups. It provides a cationic charge at acidic pH, supports the destabilization of colloidal suspension, and promotes rapid-settling, large floc. Since Chitosan is a long-chain polymer with positive charges, it can also coagulate negatively charged particulate and colloidal materials via adsorption and hydrophobic flocculation (Roussy et al., 2005; Saranya et al., 2014; Karbassi and Heidari, 2015). Seed extracts of Nirmali (Strychnos potatorum) are anionic polyelectrolytes. It can destabilize the particles in water via inter-particle chemical bridges. Nirmali seed extract contains lipids, carbohydrates, and alkaloids. Hydroxyl groups found in the polymer chain provide adsorption sites for forming chemical bridges (Theodoro et al., 2013; Yin, 2010) and –COOH and free –OH surface groups increase the coagulation competency (Yin, 2010). Polysaccharides mixtures of galactanii and galactomannani extracted from Strychnos potatorum seeds can reduce turbidity up to 80% (Adinolfi et al., 1994). According to the study carried out by Ndabigengesere et al., 1995, Moringa extracts consist of water-soluble cationic coagulant proteins. Coagulation activity is carried out via the mechanism of charge neutralization and adsorption (Ndabigengesere et al., 1995; Theodoro et al., 2013; Table 1: Summary of functional groups and mechanism proposed for natural coagulants

<table>
<thead>
<tr>
<th>Natural coagulant</th>
<th>Source of extraction</th>
<th>Mechanism proposed</th>
<th>Functional groups</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moringa oleifera</td>
<td>leaves, flowers, seeds, roots, bark</td>
<td>Adsorption and charge neutralization</td>
<td>Starch, cationic protein, fatty acids, phenolic compounds Amines, glucose, alcoholic compounds, and carboxylate groups</td>
<td>Kumar et al., 2017; Kurniawan et al., 2020; Yin, 2010</td>
</tr>
<tr>
<td>Nirmali (Strychnos potatorum)</td>
<td>seeds</td>
<td>Inter-particle bridging</td>
<td>galactan and galactomannan</td>
<td>Vijayaraghavan et al., 2011</td>
</tr>
<tr>
<td>Cactus Musilage</td>
<td>Cactus pads</td>
<td>Adsorption and bridging coagulation method</td>
<td>D-xylose, galacturonic acid, L-arabinose, L-rhamnose, and D-galactose.</td>
<td>Vijayaraghavan et al., 2011; Yin, 2010</td>
</tr>
<tr>
<td>Chitosan</td>
<td>fungi, marine invertebrates, yeasts</td>
<td>Charge neutralization and bridging</td>
<td>N-acetyl-D-glucosamine (acetylated unit), β-(1-4)-linked D-glucosamine (deacetylated unit)</td>
<td>Saranya et al., 2014</td>
</tr>
<tr>
<td>Tannins</td>
<td>Castanea, Acacia, or Schinopsis</td>
<td>Adsorption and charge neutralization</td>
<td>Polyphenol compounds</td>
<td>Vijayaraghavan et al., 2011; Yin, 2010</td>
</tr>
</tbody>
</table>
Yin, 2010). Tannins are secondary metabolites of plants, produced from the barks, leaves, fruits, seeds regarded as a potential natural coagulant for water and wastewater treatment (Yin, 2010; Grenda et al., 2020). These polyphenol compounds are obtained from Castanea, Acacia, or Schinopsis plants. Tannins contain phenolic groups of anionic nature. These phenolic groups can be deprotonated, and form phenoxide stabilized resonance, allowing coagulation (Özacar and Şengil, 2003; Yin, 2010). The effectiveness of tannin as an eco-friendly coagulant depends on the chemical structure of the extracted tannins and their degree of modification. If more phenolic groups are available in a tannin structure, the coagulation capability will increase (Yin, 2010). The high coagulation ability of the cactus is due to the presence of mucilage. It assumes as sticky and complex carbohydrates. Surface cactus pads have high water retention capability. Cactus mucilage is made up of galacturonic acid, galactose, arabinose, xylose, and irhamnose. It is stored in internal and external parts of the cactus (Saenz et al., 2004; Theodorou et al., 2013). According to Miller et al., 2008, cactus mucilage coagulation occurs by forming chemical bridges via hydrogen bonds or dipole interactions. Polygalacturonic acid present in mucilage is responsible for forming chemical bridges (Miller et al., 2008). Polygalacturonic acid structure consisted of an anionic chain, Chemisorption is involved between the charged particles and –OH and –COOH groups due to their partial de-protonation in aqueous solutions (Theodorou et al., 2013; Yin, 2010).

Types of natural coagulants

The natural coagulants have characteristics that are not noxious to an aquatic environment. It includes microbial polysaccharides (Saleem and Bachmann, 2019), bio-wastes (Atchudan et al., 2020), alginate, gelatin, cellulose-based materials, and Chitosan (Vigneshwaran et al., 2020). Most of the natural coagulants are polysaccharides; hence they are also termed polymeric coagulants. According to the origin, natural coagulants can be divided into three categories, as shown in Table 2.

Animal-based natural coagulants

Chitosan (CS) is a linear copolymer produced by the deacetylation of chitin (Verma et al., 2012). Chitosan offers several advantages over traditional compounds. For example, it is widely available (higher after cellulose), sustainable, cost-effective, non-toxic, biodegradable, biocompatible, soluble in weak acids, pH-sensitive (Martau et al., 2019; Pontius, 2016), better biosorption, no secondary pollution, sludge can reuse as agricultural fertilizer etc. (Abreu et al., 2020; Huang et al., 2000). In addition, Chitosan is efficient in reducing chemical oxygen demand, suspended solids, and turbidity (Abdullah and Jaeel, 2019).

Plant-based natural coagulants

The use of natural plant extracts dates back to 2000 BC, where Egyptians have inscribed the evidence of plant materials used for water treatment (Sivaranjani and Rakshit, 2016). According to Fatombi et al., 2013, it is clear that nuts such as beans, almonds, and Styrchnos potatorum were used in Sudan, Egypt, and India, respectively. These nuts are reported to stimulate the coagulation of turbid waters (Fatombi et al., 2013). Since the late 1970s, various plant-based polyelectrolytes and polymers have been researched as coagulants. Plant-based coagulants are generally derived from the various parts of the plants and are organic, water-soluble, ionic, and non-ionic polymers in nature (Bodlund et al., 2014; Dezfooli et al., 2016; Fatombi et al., 2013). In the colloid-free aqueous state and the colloidal particle solution consisting of restricted irreversible loop arrangements, they maintain random configurations and help in destabilization by forming micro or macro flocs through charge neutralization (Hameed et al., 2016). Some plant-based materials may also behave as flocculant by strengthening the flocs for better settleability (Al-Hamadani et al., 2011; Awang and Aziz, 2012). Several works of literature have reported applying plant-based coagulants for water and wastewater treatment (Kansal and Kumari, 2014; Kristianto, 2017; Oladoja et al., 2017). Most of the investigated coagulants are from family Fabaceae, primarily extracted from the leaves (Rak et al., 2012)

<table>
<thead>
<tr>
<th>Table 2: Types of natural coagulants</th>
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<tbody>
<tr>
<td><strong>Plant-based</strong></td>
</tr>
<tr>
<td>Moringa Oleifera</td>
</tr>
<tr>
<td>Cactus</td>
</tr>
<tr>
<td>Nirmali seeds</td>
</tr>
<tr>
<td>Tannin</td>
</tr>
<tr>
<td>Potato starch</td>
</tr>
<tr>
<td>Banana peel</td>
</tr>
<tr>
<td>Common beans</td>
</tr>
<tr>
<td>Tamarind seeds</td>
</tr>
</tbody>
</table>


and seeds (Jayalakshmi et al., 2017). One of the most popular and extensively researched plant-based coagulants is *Moringa oleifera* belonging to the family *Moringaceae* (Baptista et al., 2017; Camacho et al., 2017). The other common coagulants are Nirmali seeds, Tannins, Roselle seeds, Hyacinth bean etc, which have been studied for turbidity reduction (Saharudin et al., 2014; Fermino et al., 2017; Choubey et al., 2012). As in Table 3 is shown, they are low cost, non-toxic, locally available, readily implementable, and show great potential. Plant-based coagulants are advantageous because i) They are not dependent on chemicals; ii) they generate smaller amounts of sludge and biodegradable; and (iii) less toxic and not corrosive (Rocha et al., 2019).

Many wastewater treatments have substituted chemical coagulants with plant-based coagulants because of their low price, abundant source, multipurpose, and biodegradability (Othmani et al., 2020).

**Comparison of natural coagulants efficiency**

The list of plant-based coagulants studied as natural coagulants are summarized in Table 4, with brief accounts of their optimal conditions, applications, and efficiencies. Roselle seeds (*Hibiscus sabdariffa*) were high in proteins (28 %) and soluble in water. When in solution, they carry an overall positive charge. These positively charged proteins bind to the turbidity causing negatively charged particles in the solution. According to the research, rosselle seeds’ highest turbidity removal efficiency is within 77 % - 87 % for synthetic wastewater at pH 10 and 81 % - 93 % at pH 4 (Saharudin and Nithyanandam, 2014). *Moringa oleifera* has been one of the best plant extracts for water purification. It is effective in removing Biological Oxygen Demand (BOD), turbidity, Chemical Oxygen Demand (COD), total coliforms removal, algal removal, Hardness, Total dissolved solids (TDS), and Total suspended solids (TSS) etc. According to the research carried out by (Choubey et al., 2012), *Moringa oleifera* removes turbidity from 100 NTU to 5.9 NTU and after dosing, and filtration to 5 NTU and total coliform remove by 96 % in synthetic raw water. Furthermore, in laundry, wastewater turbidity removed by 84 % and COD by 46% (Al-Gheethi et al., 2017). In Municipal wastewater, the reduction of turbidity, COD, BOD, hardness, TSS, and TDS are found to be 61 %, 65 %, 55 %, 25 %, 69 %, and 68%, respectively (Kumar Kaushal and Goyal, 2019). Hyacinth bean (*Dolichos lablab*) peels are characterized for usage as a protein source. Hyacinth bean peels have a moderate concentration of protein. Turbidity removal efficiency is 99% with the dosage of 20 mg/L in synthetic water (Bs and Papegowda, 2012).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon footprint</td>
<td>Environmentally friendly</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Less toxic</td>
</tr>
<tr>
<td>Heavy Metals</td>
<td>Settling will occur along with the coagulation process</td>
</tr>
<tr>
<td>Sludge</td>
<td>Sludge volume/amount reduction, Low sludge handling cost, and treatment cost with good biodegradability</td>
</tr>
</tbody>
</table>

With the 200 mg/500 ml dosage, turbidity removes from 100 NTU (Nephelometric Turbidity Units) to 11.1 NTU and after dosing, filtration to 9.5 NTU, and total coliform removal 89% in synthetic water (Choubey et al., 2012). *Cactus* is another efficient natural coagulant. According to various research studies, cactus species prove efficient in removing turbidity, COD, and color. For example, in textile wastewaters, cactus removes turbidity by 92 %, COD by 89 %, and color by 99 % at the dosage of 40 mg/L and pH 7.25 (Bouatay and Mhenni, 2014). *Nirmali seeds* are another crucial natural coagulant used to remove turbidity and total suspended solids (TSS). It removes TSS by 76%, turbidity by 96% in laundry wastewater (Mohan, 2014). *Watermelon* (*Citrullus lanatus*) is the latest approach in developing an effective natural coagulant. The efficiency of turbidity removal was 88 % for the tannery effluent and 98% for synthetic wastewater. The other physicochemical parameters of tannery wastewater, such as TSS, BOD, and COD, were also reduced significantly. The COD removal efficiency was 50%, and the BOD of the wastewater was reduced by 55%. When employed as a coagulant, the watermelon seeds significantly decrease the synthetic wastewater’s TSS, turbidity, BOD, and COD, and the tannery effluent (Sathish et al., 2018).

Table 4 summarizes the facts on potential applications of plant-based materials that can be used as natural coagulants. This is significant in developing new mixed natural coagulants which deliver maximum efficiency.

Therefore, it can be said that natural coagulants have found their diverse application not only for physical and biological water and wastewater treatment but also as a disinfectant. From a
Table 4: Summary of the removal efficiencies of some natural coagulants for water and wastewater treatment

<table>
<thead>
<tr>
<th>Natural coagulant/Industrial wastewater</th>
<th>Wastewater source</th>
<th>Optimal Conditions</th>
<th>Performance Parameters</th>
<th>Removal Efficiencies</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hibiscus sabdariffa (Roselle seed extract)</td>
<td>Glove manufacturing wastewater</td>
<td>60 mg/L 10 ≤</td>
<td>Turbidity</td>
<td>87%</td>
<td>Saharudin and Nithyanandam, 2014</td>
</tr>
<tr>
<td>Moringa oleifera (Drumstick Tree)</td>
<td>Laundry wastewater</td>
<td>120 mg/L 5.7</td>
<td>COD Turbidity</td>
<td>43% 84%</td>
<td>Al-Gheethi et al., 2017</td>
</tr>
<tr>
<td>Opuntia ficus indica (Cactus species)</td>
<td>Textile wastewater</td>
<td>40 mg/L 7.25</td>
<td>Turbidity COD Color Turbidity</td>
<td>92% 89% 99%</td>
<td>Bouatay and Mhenni, 2014</td>
</tr>
<tr>
<td>Citrullus lanatus (Seeds of Water Melon)</td>
<td>Tannery wastewater</td>
<td>2000 mg/L -</td>
<td>BOD COD Turbidity TSS</td>
<td>55% 50% 69%</td>
<td>Sathish et al., 2018</td>
</tr>
<tr>
<td>Strychnos potatorum (Nirmali seeds)</td>
<td>Laundry wastewater</td>
<td>8000 mg/L -</td>
<td>Turbidity TSS</td>
<td>96% 76%</td>
<td>Mohan, 2014</td>
</tr>
<tr>
<td>Ocimum basilicum (Basil)</td>
<td>Textile wastewater</td>
<td>1600 mg/L 8.5</td>
<td>COD CO Color Turbidity</td>
<td>62% 69% 95%</td>
<td>Shamsnejati et al., 2015</td>
</tr>
<tr>
<td>Corchorus Olitorius L. (Jute mallow)</td>
<td>Agricultural wastewater</td>
<td>3 mg/L -</td>
<td>TOC (Total organic carbon) BOD COD Cl- Sulphate TDS Ni TSS</td>
<td>100%</td>
<td>Althaer et al., 2016</td>
</tr>
<tr>
<td>Bamboo (Bambusa vulgaris)</td>
<td>Electroplating industry wastewater</td>
<td>1500 mg/L 5.5</td>
<td>-</td>
<td>-</td>
<td>Sivakumar et al., 2018</td>
</tr>
<tr>
<td>Cassia obtusifolia (Sickle pod seed gum)</td>
<td>Raw pulp and paper mill effluent</td>
<td>750 mg/L 5</td>
<td>TSS COD</td>
<td>87% 36%</td>
<td>Subramonian et al., 2014</td>
</tr>
<tr>
<td>Pectin of orange peel pith</td>
<td>Surfactant</td>
<td>8000 mg/L -</td>
<td>Turbidity TSS</td>
<td>90% 82% 99%</td>
<td>Mohan, 2014</td>
</tr>
<tr>
<td>Dragon fruit foliage</td>
<td>Concentrated latex effluent</td>
<td>800 mg/L 10</td>
<td>Turbidity</td>
<td>95% 89% 99%</td>
<td>Idris et al., 2012</td>
</tr>
<tr>
<td>Papaya Seed</td>
<td>Textile wastewater</td>
<td>570 mg/L 2</td>
<td>Color</td>
<td>85%</td>
<td>Kristianto et al., 2018</td>
</tr>
<tr>
<td>Olive mill wastewater</td>
<td></td>
<td>400 mg/L -</td>
<td>TSS Turbidity</td>
<td>81% 84%</td>
<td>Rizzo et al., 2008</td>
</tr>
<tr>
<td>Paper and pulp wastewater</td>
<td></td>
<td>1800 mg/L -</td>
<td>COD</td>
<td>93%</td>
<td>Thirugnanasambandam et al., 2014</td>
</tr>
<tr>
<td>Chitosan</td>
<td>Brewery wastewater</td>
<td>120 mg/L -</td>
<td>COD TSS Turbidity</td>
<td>50% 73% 95%</td>
<td>Gautam and Saini, 2020</td>
</tr>
<tr>
<td>Textile wastewater</td>
<td></td>
<td>30 mg/L -</td>
<td>Turbidity COD Cr(VI) TDS TSS</td>
<td>95% 65% 96% 92%</td>
<td>Hassan et al., 2009</td>
</tr>
<tr>
<td>Aspergillus niger</td>
<td>Tannery industry wastewater</td>
<td>4.0 g 3</td>
<td>Turbidity</td>
<td>98% 95% 90% 94%</td>
<td>Sivakumar, 2016</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anionic coagulant</th>
<th>Wastewater source</th>
<th>Optimal Conditions</th>
<th>Performance Parameters</th>
<th>Removal Efficiencies</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moringa oleifera (Drumstick Tree)</td>
<td>sewage, gray water (water from sinks and showers)</td>
<td>- -</td>
<td>Turbidity COD BOD TSS TDS</td>
<td>61% 65% 55% 69% 68%</td>
<td>Kumar Kaushal and Goyal, 2019</td>
</tr>
<tr>
<td>Citrullus lanatus (Seeds of Water Melon)</td>
<td>Sewage wastewater</td>
<td>72.3 mg/L 5</td>
<td>BOD TSS</td>
<td>92% 93%</td>
<td>Joaquin et al., 2021</td>
</tr>
<tr>
<td>Cucumis melo (Cantaloupe seeds)</td>
<td>sewage, gray water (water from sinks and showers)</td>
<td>76.7 mg/L 7</td>
<td>BOD TSS</td>
<td>80% 88%</td>
<td>Kumar Kaushal and Goyal, 2019</td>
</tr>
</tbody>
</table>
Continued Table 4: Summary of the removal efficiencies of some natural coagulants for water and wastewater treatment

<table>
<thead>
<tr>
<th>Natural coagulants for water and wastewater</th>
<th>COD</th>
<th>TDS</th>
<th>TSS</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morphina oleifera (Drumstick Tree)</td>
<td>67%</td>
<td>69%</td>
<td>72%</td>
<td>30%</td>
</tr>
<tr>
<td>Dolichos lablab (Hyacinth bean)</td>
<td>89%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cicer arietinum (Chickpea)</td>
<td>96%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opuntia ficus indica (Cactus species)</td>
<td>89%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mango pith</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trigonella foenum-graecum (Fenugreek seeds)</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citrullus lanatus (Seeds of Water Melon)</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jatropha curcas (Cactus species)</td>
<td>99%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mango pith</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trigonella foenum-graecum (Fenugreek seeds)</td>
<td>98%</td>
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</tr>
<tr>
<td>Citrullus lanatus (Seeds of Water Melon)</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jatropha curcas (Cactus species)</td>
<td>99%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mango pith</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moringa oleifera (Drumstick Tree)</td>
<td>65%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cassia alata (Christmas candles)</td>
<td>97%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opuntia dillenii (Cactus species)</td>
<td>93%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prunus armeniaca (Apricot)</td>
<td>56%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mangifera indica, (Mango)</td>
<td>68%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tannin</td>
<td>80%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Banana pith</td>
<td>99%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The table continues with more entries for natural coagulants and their removal efficiencies for water and wastewater treatment.
disinfection point of view, comparing the chemical and natural coagulants is interesting, considering their different parameters during usage. The natural coagulants are biodegradable and have no toxic effect on the receiving water bodies, which is a significant issue for chemically disinfected waters. Moreover, compared to chemical coagulants, the natural coagulants generally are readily available and generally sourced from the local areas making an attractive alternative as a disinfectant, which eliminates the need for storage in a controlled room. A study by Amran et al. (2018) has also emphasized on the need to conduct more detailed studies on the efficiency of plant-based coagulants for water and wastewater treatment. Therefore, detailed studies are required to explore its possibilities as a disinfectant for commercial purposes.

Natural coagulants - barriers for the commercialization

Most natural extracts have proven their coagulation capabilities in removing COD, BOD, TSS, turbidity, etc.; not many have accepted and reached commercialization. Four main barriers hinder commercialization: Financial capability, regulatory approval, market awareness, and research development (Choy et al., 2014). Another study by Saleem and Bachmann (2019) has highlighted the coagulants’ cationic, anionic, and non-ionic nature and explored its application and commercialization constraints. The existing research outcomes are mostly confined to laboratory scale, lacking in real industrial applications. Lacking financial freedom and understanding about the market hinder the investors from investing in a new product. Economically feasible extraction methods are essential for successful commercialization. Comprehensive studies on the coagulation mechanism are also limited. Approval from the local government authorities and other regulatory authorities must be granted to launch any new products successfully. Obtaining approval is not easy without ensuring product compliance to the respective standards. Strong motivation for green chemistry concepts and cleaner production of the investors are crucial for the natural coagulant development and their applications. Table 5 summarizes the barriers that affect the successful commercialization of natural coagulants.

The main barrier for the commercialization of natural coagulants is difficulty in bulk production of raw materials; plant species. Raw materials used to produce chemical coagulants such as aluminum, iron are abundant in nature. For a successful and realistic application, raw materials required to produce natural coagulant should be available in large scale. Technical support, expert support and new equipment are necessary in sustainable implementation of natural coagulants so that production cost will ultimately increase. In short run this is not very economical so that market acceptance will be less. Hence the absence of mass plantation of recourses hiders steady supply of raw materials and the long term applications (Kurniawan et al., 2020). As Table 5 shows, natural coagulants are not readily available. Plant materials pass few stages before convert in to a plant-based

Table 5: Barriers in the commercialization of natural coagulants

<table>
<thead>
<tr>
<th>Environmental and Technical Constraints</th>
<th>Economic and Social Constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Complex extraction process</td>
<td>• Lack of money and time to invest in research and development.</td>
</tr>
<tr>
<td>• Absence of mass plantation for bulk processing</td>
<td>• Lack of maintaining a steady supply of raw materials.</td>
</tr>
<tr>
<td>• Due to the organic properties of natural coagulants, COD levels might increase.</td>
<td>• Lack of meeting the minimum quality requirement.</td>
</tr>
<tr>
<td>• Lack of toxicological studies for purified coagulants.</td>
<td>• Lack of regulatory approvals on plant-based coagulants.</td>
</tr>
<tr>
<td>• Seasonal variations in some plant resources. (Cactus grow in hot seasons)</td>
<td>• Lack of awareness and market interest.</td>
</tr>
<tr>
<td>• Lack of research regarding the practical usage and issues occurring during the operations within the plant</td>
<td>• Well established, competitive market.</td>
</tr>
<tr>
<td>• Lack of proper arrangements for storage of the natural coagulants in stock.</td>
<td>• High initial establishment cost.</td>
</tr>
<tr>
<td>• Improper estimation of the quality characteristics of the treated water</td>
<td>• Industrial acceptance</td>
</tr>
<tr>
<td>• Lack of proper arrangements for storage of the natural coagulants in stock.</td>
<td>• Lack of knowledge on health improvements</td>
</tr>
</tbody>
</table>
natural coagulant. These stages includes: extraction of active compound, purification etc. Extraction processes are different form plant- based to animal-based coagulants. Hence these processes should be carefully analyzed and should produce simplified and economically feasible processing steps. So that further studies needed to be carried out to analyze the converting and handling of powdered forms of coagulants, storing and preservation as well as toxicity (Kurniawan et al., 2020). Therefore commercialization process is costly as well as may take more time than expected. As mentioned in Fig. 1 coagulation process depends on coagulant type and dosage, pH, temperature etc. Hence these parameters should be optimized before implementing to the industry and it is more time consuming so that it will be difficult to cope with the competitive market (Kurniawan et al., 2020). Government and non-government regulatory bodies should encourage the industry to use natural coagulants in wastewater treatment process by implementing environmental rules (Freitas et al., 2018; Kurniawan et al., 2020) and reducing tax payments (Kurniawan et al., 2020), introduce new loan schemes to cover the initial implementation costs, linking the connection between research organization and industry and give recognition for the use of natural coagulants. Due to the use of high optimal dosages of natural coagulants, high amounts of residual organic matter (Freitas et al., 2018; Oladoja, 2016) is found in treated wastewater hence the COD levels will increase. This will ultimately increase the microbial activity leading to change in color and emission of unpleasant odors (Kurniawan et al., 2020; Oladoja, 2015). When selecting a plant species as raw material for the production of natural coagulants, it is important to consider their seasonal variations and availability (Kurniawan et al., 2020). Hence research and development studies should be conducted to identify best, economically productive natural coagulants and also to identify feasible combinations of chemical and natural coagulants.

Modified natural coagulants

A breakthrough in the commercial profit-oriented market can be made by emphasizing the need for blended coagulants. Lately, Mohd-Salleh et al., (2019) indicated natural materials as aids for future coagulant production and discussed the potential to develop composite coagulants that are sustainable. Natural coagulants can be used in conjunction with modifying agents. Table 6 shows some of the modifying agents used in combination with natural coagulants. Many of them are also active as flocculants when combined with a modifying agent. Chitosan is biodegradable and eco-friendly in comparison with traditional coagulants and acts as a bio-flocculant. It is used as a substitute for conventional coagulants in water treatment. Chitosan has primary amino groups; these amino groups can remove various contaminants. Previous studies have shown that Chitosan removed around 99% of Microcystis aeruginosa cells. However, its low production yield leading to a high cost of operation has hindered its application as a sole coagulant in practical scenarios (Ma et al., 2016). Due to its insolubility in neutral and alkaline conditions, the application of Chitosan is usually limited. Chemically modified chitosan materials have been manufactured to overcome this issue (Dharani and Balasubramanian, 2015; Zhang et al., 2014). According to the study (Vigneshwaran et al., 2020), Moringa seeds are considered natural coagulants/floculents. It is mainly comprised of lipids and protein. The protein molecules of moringa seeds can bridge –NH₂ groups and –OH groups present in the chitosan molecule. Bridging will leads to the destabilization and aggregation of the small stable colloidal impurities into larger particle units. Hence, it is known as floc. The floc can remove through several physicochemical processes such as solid-liquid separation, slow mixing, and rapid mixing (Vigneshwaran et al., 2020). Recently, natural polymeric coagulants, such as cellulose, Chitosan, starch, have drawn more attention due to their advantages of low price, biodegradability, vast resources, and low toxicity. In addition, attention was focused on starch-based coagulants because starch is one of the most abundant natural polymers globally and has been applied in various fields (Li et al., 2015).

According to Ma et al., 2016 dual coagulant prepared by using chitosan and aluminum chloride is efficient in removing toxic cyanobacteria Microcystis aeruginosa found in water bodies. This novel mixed coagulant shows a strong bridging ability and high adsorption. This study suggests that CTASC is efficient, cost-effective, specific, and safe in removing Microcystis aeruginosa. Zhang et al., 2014, mentioned chitosan-based flocculent N-carboxyethylated chitosan (CEC) is eco-friendly coagulant produced by chitosan and acrylic acid. It flocculates copper (II) and tetracycline (TC). The advantages are in the aspects of optimal dosage,
The charge neutralization mechanism is used for the removal of copper (II), and TC makes a coordination complex with copper(II) hydroxides and eliminates with copper (II) at pH 9. Mercapto-acetyl chitosan (MAC) is prepared by combining mercaptoacetic acid and chitosan. It has the ability of adsorption bridging so that water solubility is high (Zhang et al., 2015).

Turbidity is removed by electrical neutralization of the turbidity substances. Heavy metal ions produce coordination complexes or chelate with MAC and form flocs (Zhang et al., 2015). According to Dharani and Balasubramanian, 2015 study, Chitosan-g-N-MPC is prepared by grafting N-methyl piperazinium chloride to chitosan. Flocculation mechanisms are charge neutralization and bridging. Due to the considerable molecular weight and high charge density, it requires low optimal dosages. According to Vigneshwaran et al., 2020, acid-treated carbonized chitosan-Moringa oleifera (ACCM) shows better adsorption ability, high coagulation capability, low sludge formation and low leaching level. Coagulation mechanisms are charge neutralization and adsorption. Li et al., 2015 discussed two kinds of starch-based flocculants. Though they have the same chemically modified functional groups, substitution degrees are different. CMS-CTA-P and CMS-CTA-N have opposite surface charge properties in water. CMS-CTA-N is efficient in the hematite suspension at neutral conditions. CMS-CTA-P shows a better flocculation activity in the kaolin suspension at neutral and acidic conditions. Patching, bridging, and charge neutralization are found as flocculation mechanisms.

**CONCLUSION**

Coagulants obtained from many natural sources have found their place in the water and wastewater industry world and are widely being used as primary coagulants or coagulant aids. Natural coagulants are environmentally friendly, inexpensive, less hazardous to human beings, and viable alternatives to chemical coagulants. Plant-based, animal-based, and microorganism-based coagulants have been researched for ages and have become popular in developing countries. This review summarized the efficiencies of common natural coagulants such as Roselle seeds, Moringa oleifera, Hyacinth bean, Cactus, Nirmali, Chitosan, Tannins and Watermelon seeds etc., used in the water and wastewater treatment and suggested that plant-based species showed good efficiencies in removing turbidity, color, organic matters as well as pathogens. It was noticed that many studies had investigated the application of plant-based coagulants in the primary treatment.
for turbidity removal and secondary treatment for organic pollutant (TSS, BOD, and COD) removal. However, its disinfection aspect is not well explored. Studying the plant-based coagulants or plant species for the tertiary treatment of water and wastewater could be an exciting area for future research. Further, plant-based coagulants are advantageous due to their low toxicity and eco-friendly sludge production. Despite having significant benefits, some crucial barriers to the commercialization of natural coagulants are identified in this review. The significant barriers are environmental, technical, economic, and social challenges. However, there have been efforts made to commercialize natural coagulants through modified natural coagulants. There are two modified coagulants summarized in this work: Chitosan and starch, which are considered an alternative way to enhance the efficiency of the coagulants and increase its market demand. The concept of modified or composite coagulants could be taken as an indirect example for tackling these constraints. However, there are limited studies on these barriers, and this review recommends that more investigations and assessment methods are required to find the origin of these constraints and solve it through more scientific approaches. Further, from a sustainability perspective, the demand for natural coagulants is destined to increase. Therefore, more researches in the modified coagulants hold promising prospects.

AUTHOR CONTRIBUTIONS

S. Nimesha has done most of the writing and preparing the manuscript. C. Hewawasam has done some part of writing, editing and supervision of works of first author. D.J. Jayasanka has done some part of writing, editing and supervision of works of first author. Y. Murakami is the advisor for the writing this review. N. Araki is the advisor for this research work. N. Maharjan has given significant intellectual inputs and supervised this work.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, ethical issues, including plagiarism, informed consent, misconduct, data fabrication and falsification, double publication and submission, and redundancy, have been entirely witnessed by the authors.

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ABBREVIATIONS

AC
Aluminum chloride
ACCM
Acid treated carbonized chitosan-Moringa oleifera
AD
Alzheimer’s disease
BOD
Biological oxygen demand
CEC
Carboxy-ethyl Chitosan
Chitosan-g-N
N-methyl piperazinium chloride grafted Chitosan
CMS-CTA-P / CMS-CTA-N
(2 hydroxypropyls) trimethylammonium chloride etherified carboxymethyl starch (two different substitution degrees)
COD
Chemical oxygen demand
-COOH
Carboxyl group


Cr, Chromium
CS, Chitosan
CTS, Chitosan to be modified
CTS-AC, Chitosan -aluminum chloride
Cu, Copper
Fe, Iron
g, Grams
MAC, Mercapto - acetyl chitosan
mg/L, Miligrams per liter
Mn, Manganese
-NH₂, Amine group
Ni, Nickel
NTU, Nephelometric turbidity units
-OH, Hydroxyl group
Pb, Lead
pH, Potential (power) of hydrogen
TC, Tetracycline
TDS, Total dissolved solids
TOC, Total organic carbon
TS, Total solids
TSS, Total suspended solids
Zn, Zinc
% Percentage sign

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