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ENHANCEMENT THE QUALITY OF TREATED EFFLUENT USING NATURAL MATERIALS AS COAGULANT: A REVIEW ARTICLE

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Abstract

Natural coagulants have proven its coagulation efficacy as reported in a significant number of research articles. However, the acceptance and massive application of natural coagulants in the water industry is still low. It is important to conduct a review to raise the potential of using natural coagulants by highlighting the efforts and the current development for refining the capability of natural coagulants, including showing the compatibility of natural coagulants with other treatment technologies in hybrid/integrated treatment procedures; the modification of natural coagulants for the possibility of hybridizing natural coagulants with additional kinds of coagulants; marked enhancement in coagulation performance efficiency; the improvement of extraction and purification methods for high purity of natural coagulants and the synthesis of multifunctional natural coagulants. However, the present progress of natural coagulants is quite encouraging, perspectives from sustainability assessment showed that the acceptance and commercialization of natural coagulants are stuck by two main challenges: feasibility and practicality of real field application and sustainability of using natural coagulants commanding technical, economic, environmental, and social aspects. Upcoming research focusing on these subjects may assist in clarifying the uncertainties shrouded on natural coagulants and at the same time modifying the water industry to be more sustainable.

Keywords: Natural coagulant, Wastewater and water treatment, Sustainability, Coagulation Hybrid Integrated.

1. Introduction

Coagulation and flocculation processes are widely used in water and wastewater treatment. Its main objective is to remove suspended colloidal particles and to reduce turbidity in water bodies [1]. The procedure usually takes place in a chemical reactor in which the influent water or wastewater enters the basin and mixed with coagulant agents using a mechanical mixer, followed by sedimentation procedure to remove the particulate through gravity settling. Coagulants are characterized according to the wastewater properties that relate to enhancing the efficiency of the treatment process to achieve the required quality of water on standards (as shown in Table 1) [2].

There are many types of coagulants available. The most often used are the chemical-based coagulants such as ferric salts and alum. However, several drawbacks of using inorganic coagulants are frequently reported. For example, the harmful voluminous sludge production and the overdosing of alum in water or in wastewater treatment may lead to a high residual aluminum concentration. In addition, the prolonged exposure to water with high residual aluminum contents linked to serious health issues, such as the development of Alzheimer's disease and senile dementia [3-6]. There are also coagulants derived from plant-based materials known as natural coagulant. Natural coagulants are safe and ecofriendly[1]. In natural coagulant, coagulants are used normally in the form of natural (as shown is Table 2). These coagulants aim to eliminate pollutants in form of physical (solids & turbidity) or chemical (BOD & COD). The coagulants also present with advantages several among them. The impact of pH and coagulant doses on the coagulation procedure was contemplated in order to streamline relating to the best evacuation of turbidity. The optimum dosage of pH will lead to the optimum conditions of JAR test. Coagulation affects the performance of the additional stages of the treatment, favoring microbiological quality of the final product, reducing the final cost of the treated water and increasing the lifetime of filters [7].

Table 1. Factors Affecting Coagulation[2]

Coagulant Applications	Effective Characteristics	Natural Water Properties
Coagulants Extraction Coagulants Solubility Coagulants Dosage Charge on Particles Basicity of a coagulant	Settling time Turbulence 1. Rapid Mixing 2. Slow Mixing Coagulant adds quantity Particles type	pH Alkalinity Availability of Bacteria's Presence of Elements (Cl, Na, Mn, Si, Fl, NH_3, Fe) Total dissolved solids Suspended Solids Temperature Turbidity Dissolved Oxygen

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Table 2. Natural coagulants Efficiency[7]

Natural Coagulants	Turbidity	COD
CicerAretinum	81.20%	90.00%
Moringa Oleifera	82.02%	83.33%
Cactus	78.54%	80.65%

Natural coagulants can be extracted from microorganisms, plants and animals. Some of the plants are able to be a coagulant because they are able to conduct some of the coagulation mechanisms that perform polymer bridging and neutralizing the charge in colloidal particles [8]. One example of natural coagulant is Okra gum. It's a natural polysaccharide made up of D-galactose, L-rhamnose and L-galacturonic acid. Water-soluble natural polysaccharides can destabilize colloidal suspensions and thus are capable of flocculating small particles and reducing turbulent drag. These properties have marked the beginning of innovative applications in wastewater treatment, agriculture and mineral beneficiation [9, 10].

1.1. Mechanism of Natural Coagulant

There are four types of coagulation mechanisms which are double layer compression, charge neutralization, polymer bridging and sweep coagulation. Though, only charge neutralization and polymer bridging are the feasible coagulations mechanisms for plant-based natural coagulant [8]. Polymer bridging is preceded by polymer adsorption which is a process where long chain polymers attach themselves to the colloidal particle's surface because of the affinity present between them. Only some part of the polymers is attached to the particle while the unattached parts will form loops and tails [11]. These loops and tails are the main structure of polymer bridging because it allows attachments to other colloidal particles and thus forming larger flocs as shown in Figure 1.

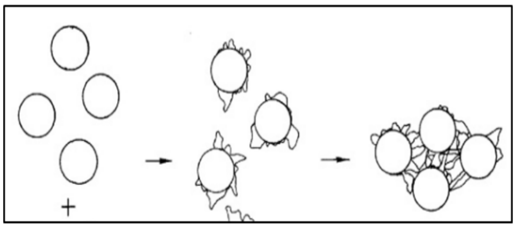

Fig. 1. The illustration of a bridging mechanism in coagulation [12]

Therefore, sufficient unoccupied particle surface is needed to gain effective polymer bridging and the bridging must span far enough to overcome the interparticle repulsion. These conditions are met by adding sufficient dosage of polymer through natural coagulant which provides enough bridging links and bare particle surface for strong polymer bridging [12]. The charge neutralization mechanism uses ionizable polymer (polyelectrolytes) as coagulant to stabilize the colloidal particle. Colloidal particles are negatively charged and that causes them to repel one another. Therefore, polycations are used to stabilize the particles, gaining near to zero zeta potential. Charge density of the polyelectrolyte will determine the optimum dosage of polyelectrolyte needed because higher charge density corresponds to lower coagulant dosage [11]. The basis of charge neutralization is that the adsorption of high charge density polyelectrolytes by low charge density colloidal particles occurs in a 'patch wise' manner. This is called electrostatic patch mechanism (Figure 2), meaning that the particle's surface has patches of positive and negative regions. These regions cause additional attraction between particles given that the opposite charged regions are properly aligned.

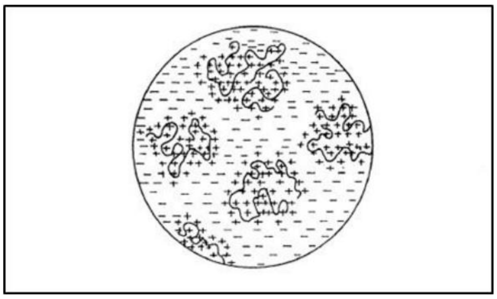

Fig. 2. The electrostatic patch model in a charge neutralization mechanism [12]

1.2. Processing Steps of Natural Coagulants

The first processing phase is widely and essential for conjugal application for utilization. In this step plant is cut, sliced, choped and peel for drying purpose by manual or mechanical pulverization to avoid undesired parts. The conventional method involves aeration and following pulp of plant parts into particles that are then used by local area due to lack of such equipment. In the second processing phase, organic and/or alcoholic solvents extraction is used to remove the active agents. However, water & salt solution (NaCl) extraction [13, 14] also used. The previous research pointed out that by using NaCl solution extraction with lower dosages as 7.4 times higher to eliminate kaolinite turbidity. The third process phase involves dialysis, lyophilization, ion-exchange and precipitation to treat water as viable refining methods for *Moringa oleifer a*s tapped for treatment of higher volumes of turbid water [15].

1.3. Advantages and Disadvantages of Natural Coagulant

Natural coagulant gains the advantage over chemical coagulant due to various reasons. One of the reasons are natural coagulant are safer than chemical coagulant. When using coagulant for water treatment, there will be a possibility of residue coagulant present in the water after the treatment. Chemical coagulant residue such as alum is harmful because it can cause Alzheimer's disease if consumed [16]. On the other hand, if natural coagulant was used, the residual coagulant would not be harmful. Likewise, natural coagulant is much cheaper compared to chemical coagulant. Chemical coagulant such as alum, need coagulant aid to effectively treat high turbidity water, thus making it more expensive and difficult to be used in poor countries. Whereas natural coagulants are much cheaper and can be extracted from various plant wastes which greatly reduces the treatment cost [17]. Nevertheless, an abundance and locally available resources must be met to use natural coagulants commercially. Natural coagulant also has some disadvantages. Using natural coagulant will increase the organic matter present in the water, thus increasing microbial activity. Consequently, additional chlorine should be used to sanitize the treated water [18]. Besides that, natural coagulant such as Moringa oleifera need longer sedimentation time than chemical coagulant and although some coagulant has antibacterial property that can treat *Escherichia*. coli infested water, the removal efficiency is not complete, thus secondary bacterial growth risk could occur[19].

2. Developing natural coagulants and its related challenges in applications

In the past few years, a theory shift in water and wastewater treatment industries has changed the culture of water workers to implement and adopt sustainable development in the operation. One of the reasonable practices is to replace the chemicals used in the treatment processes with "green" chemicals that cause less important environmental impacts in terms of production, consumption, and secondary waste management. In this situation, natural coagulants look to fit into the picture and can be an option over the traditional inorganic coagulants. It has been normally reported that natural coagulants can be gained from renewable feedstock with ease, produce biodegradable sludge at minor quantity (potentially cutting down losses associated with sludge disposal), and fewer affected by water pH [20, 21]. Various review articles have reportedly supported the success of natural coagulants (mainly plant-based coagulants and chitosan) in several wastewater and water treatment applications [20-26]. These review articles also showed the extraction of natural coagulants and highlighted some of the application challenges of natural coagulants. Nonetheless, the acceptance of natural coagulants in real wastewater and water treatment plants is low. The commercialization of natural coagulants has faced few critical challenges that delay its transition from bench-scale coagulation study or lab to extensive actual wastewater and water treatment application. The main problem is the lack of industrial confidence to adopt natural coagulants in the treatment procedures. However, the benefits and performance of natural coagulants as mentioned above have been confirmed in bench-scale studies or lab, concern arises about its performance consistency and cost-effectiveness in actual treatment procedures. In some articles, the dosage of natural coagulants was less than conventional coagulants. In contrast, several articles have revealed that to get the corresponding performance (impurities removal) as conventional coagulants (inorganic coagulants), a larger dose of natural coagulants is required due to its weaker coagulation capability [27-29]. This could possibly be linked in extra costs associated with the increase of dosage consumption, such as extraction, storage, transportation, and treatment of natural coagulants. In view of this, worries have arisen over practical use and the claim of natural coagulants as an alternate compound for sustainable development. To explain these uncertainties, and to increase the confidence of acceptance of natural coagulants, the practices and signs of progress that could showcase the usefulness and value of natural coagulants should be explored. Unfortunately, a considerable number of research articles have focused only on performance evaluation study. Hence, this chapter (Literature Review) aims to investigate this matter and highlight what has been done in academia that could improve the perception towards natural coagulants in water and wastewater treatment application. These will be discussed in a few sections as follows modification of natural coagulants for improved performance; application of natural coagulants in integrated/hybrid procedure; hybridization of natural coagulants with other types of coagulants; the synthesis of multifunctional coagulants; and improvement of extraction and purification of natural coagulants. In addition, in alignment with the sustainable development goals, the sustainability aspects of natural coagulants application will be discussed.

3. Improvement in natural coagulants

3.1. Integrated/hybrid process.

One of the viable strategies to increase the use and to show the usefulness of natural coagulants is to integrate it with other treatment technologies, just like the integration of traditional inorganic coagulants with other processes. The common practice in water and wastewater treatment plants is to integrate various technologies to achieve the treatment goals by employing the strength of each process and to minimize the shortcomings of others. A similar approach can be adopted where the coagulation process (using natural coagulants) can be integrated to improve the effectiveness of subsequent treatment processes at par with conventional inorganic coagulants. The biological treatment unit is an indispensable process in a typical municipal wastewater treatment plant. Efforts have been made to reduce the working volume and demand for oxygen (energy through aeration requirement) for better treatment efficiency. One of the techniques is to decrease the organic load in the wastewater through coagulation process. Hameed, Idris [30] incorporated coagulation and flocculation prior the conventional biological treatment procedure by employing Tanfloc, a commercialized tannin based coagulant (Hameed, Idris [30]. It was shown that coagulation process enhanced the removal efficiency of the primary clarifier by agglomerating the suspended solids for sedimentation. With the decline of organic load, the dissolved oxygen level in aeration tank had doubled, indicating the opportunity for cost-saving through lower aeration requirement or the use of smaller air blower. This demonstrates that natural coagulants are beneficial as conventional inorganic coagulants as pretreatment in increasing the performance of subsequent treatment processes. Coagulation has been regularly adopted as pre-treatment prior to membrane filtration process with the intention to mitigate membrane fouling issues. Several articles of integrated coagulation-membrane procedure have been reported with positive outcomes, where the membrane fouling propensities have been successfully reduced [31]. However, natural coagulants can perform well in removing the foulants which are responsible for membrane fouling, there are a few worries that need to be considered when performing such integrated process. Chitosan natural coagulant reportedly improved the fouling propensity of nanofiltration membrane towards the natural organic matter, while the mitigation efficiency was not as good as ferric chloride inorganic coagulant [32]. This could be attributed to the charge neutralization as the predominant mechanism for chitosan coagulation that produced neutrally charged particles and subsequently weakened the antifouling capability (electrostatic repulsion) of membrane. On the other hand, Katalo, Okuda [28] reported that there was no clear difference in membrane fouling propensity for a microfiltration procedure receiving supernatant from Alum coagulation or Moringa oleifera, even though the turbidity removal efficiency of the latter was better [28]. The use of Moringa oleifera slightly increased the load of organics in the treated river water, yet its advantage over alum coagulant was that the water pH did not vary much after the coagulation process, saving the need for pH adjustment after the treatment process. All these showed that even though natural coagulants possess the potential as an alternative coagulant to mitigate membrane fouling, its compatibility and impacts with the water sources and membrane performance should be properly studied before decision is made. Barbosa, da Silva [33] showed that Moringa oleifera extracted from the seeds was capable of treating the water-based paint wastewater and render it suitable for reuse in the plant [33]. Interestingly, the quality of the treated water using Moringa oleifera was on par with the treated water using aluminum sulphate (inorganic coagulant). Integrating the electrolysis procedure with coagulation further refined the quality of the supernatant (by degrading the organic compounds in the effluent), making it suitable for discharge into water bodies. This case study indicated that by integrating the coagulation with other treatment knowledge, the quality of the treated industrial wastewater can be further improved to be safely discharged to the environment in compliance with regulations. Solar disinfection is a feasible process that could provide drinking water in the rural communities of developing countries. Though, solar disinfection only does not result in complete disinfection of microorganism, generally due to the turbidity (organic matters and suspended) in water that blocks the penetration of ultraviolet radiation in water and leads to low bacterial inactivation. To resolve this matter, Megersa, Gach [29] employed extracts from plants as natural coagulants (Maerua subcordata and Moringa stenopetala) to decrease the turbidity through coagulation procedure [29]. The results revealed that with the use of coagulants previous to the solar disinfection procedure, complete bacterial inactivation was achieved. This could be attributed to the exclusion of turbidity that increased the penetration of ultraviolet rays which killed off the bacteria in water sources. Such case shows that natural coagulants can be useful in the effort to supply adequate and clean drinking water in the rural communities, where the natural coagulants can be obtained locally and easily, without having the logistic and financial constraints of using inorganic coagulants. Adjeroud, Elabbas [34] showed that the inclusion of Opuntia ficus indica natural coagulant in the elecrocoagulation-electroflotation practice assisted to reach 100% copper removal efficiency (100 mg/L) in a shorter operating duration [34]. The natural coagulant provided a great number of hydroxyl and carboxyl groups for the enhanced deletion of copper through precipitation reaction. Apart from the improvement of pollutant removal efficiency, the addition of Opuntia ficus indica had sped up the sludge settling rate (as much as 15%) and reduced the specific energy consumption of the electrocoagulation-electroflotation procedure. The addition of natural coagulant, which consists of numerous polyelectrolytes, assisted in the removal of copper (cutting down the consumption of aluminum electrode) and reduced the ohmic resistance of the wastewater. Therefore, the natural coagulant enhanced the economic feasibility of the electrocoagulation-electroflotation procedure. Thus, it can be seen that natural coagulants can not only improve the removal of pollutants, but in specified cases can bring extra benefits as well. There is a long list of integrated procedures using natural coagulants. Mainly, Coagulation using natural coagulants can be integrated with another treatment technologies as displayed in Fig. 3.

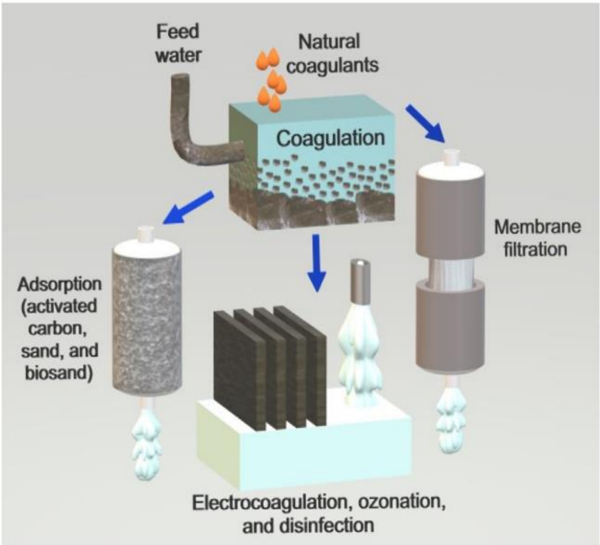

Figure 3. Integrated/hybride coagulation process (Natural coagulants) for water and wastewater treatment [35].

It can be decided that natural coagulant is as competent as conventional inorganic coagulant in the integrated process for an extensive variety of water sources (surface wastewater and water from various industrial sources). The integration of natural coagulant as pre- or post-treatment of additional treatment technologies will benefit the overall procedure, even on par with using inorganic coagulant. Pilot-scale or real application of integrated treatment processes should be explored to affirm the competency of natural coagulants.

3.2. Improvement of extraction and purification of coagulants

Normally, majority of the natural coagulants can be classified into two groups based on the main compounds with coagulation activity: proteins and polysaccharides [1, 36]. Examples of the first group are starch, chitosan, and mucilage while protein-based natural coagulants normally originated from plants (Moringa). The existence of amino and hydroxyl functional groups on these compounds contribute to coagulation ability. Unlike the regular metallic inorganic coagulants where the characteristics (quality) of the coagulants can be controlled accurately, the quality of some natural coagulants is difficult to control. Such incident could be ascribed to the green synthesis of these natural coagulants, where the coagulants are extracted through several simple procedures and sources (especially plant-based coagulants where the compounds might differ according to growth conditions). In addition, it is inevitable that non-coagulating impurities will also be included in the extracted natural coagulants if further purification is not performed. Though, extensive purification will render the "cost-saving" aspect of natural coagulants unattractive and incur extra cost. The presence of impurities that have no coagulation capability would severely affect the coagulation efficiency, as past literatures have revealed that these impurities contributed to dissolved organic substances and subsequently degraded the quality of the treated water [37, 38]. These give growth to uncertainties in quality control as the performance of the natural coagulants might differ according to the sources and extraction approaches. Then, the efficiency and varyingly quality of the natural coagulants are rather confusing and not appealing to prove the water utilities to adopt natural coagulants in their treatment processes. To clarify these matters, this section will discuss the influence on the quality and performance of natural coagulants and the improvement of extraction methods in treating wastewater and water. Moringa is one of the most popular plant-based natural coagulants that has received extensive research coverage. Several extraction approaches of useful compounds with coagulation activity from Moringa have been reported. The simplest procedure of extraction is through the use of clean water. The powdered Moringa seed kernel was mixed with water and stirred to release the coagulating compounds (positively charged proteins) from the seed kernel [39]. Though, coagulation efficiency of this extraction approach is normally unsatisfactorily due to the low number of coagulating compounds and the presence of non-coagulating impurities. Water as solvent could not extract the proteins in the seed kernel effectively. Moreover, it was reported that together with the protein compounds (with coagulation capability), the carbohydrates (impurities) and lipids would also seem in the extracted natural coagulant. Lipid content may inhibit the contact between the impurities and coagulants, rendering the flocs formation ineffective while the carbohydrates may grow the organic matter level in the solution [38, 40, 41]. Therefore, the coagulation performance from the proteins has been diminished with the adverse effects arising from the impurities. To resolve these issues, improvement in the extraction method and inclusion of purification step can be adopted. The amount of a substance's possessing coagulation capability can be increased by using salt solutions (such as $CaCl_2$ and NaCl) during extraction step [29, 42] For instance, Megersa, Gach [29] showed that the use of salt solutions (NaCl, KNO_3, and NH_4Cl) could enhance the coagulation performance as compared to the Moringa coagulant extracted with water [29]. The ideal dosage of coagulant extracted using 0.5 M NaCl solvent was 2 mg/mL with turbidity removal efficiency of 91%. In comparison, the turbidity removal performance of coagulant extracted using deionized water was much lower (37%), even though its dosage was higher (4 mg/mL). Such improvement was due to the effect of salting in as explained by Debye-Huckel theory (increasing solvating power). The presence of salt ionic strength increased the solubility of the proteins by breaking down the protein-protein bond of natural coagulants [29, 43]. Later, the quantity of active compounds with coagulation capability (proteins) in the extracted coagulants was higher when extracted using salt solutions and resulted in lower optimal dosage with improved performance. At lower coagulant dosage, the risk of residual organic compounds in treated water would also be decreased [29]. The type of solvent used in the extraction procedure would also bring extra benefits to the coagulation process. Carvalho, Alves [42] observed that Moringa coagulant extracted with CaCl2 attained higher turbidity removal efficiency as compared to NaCl solvent, which could be attributed to the participation of calcium ions in coagulation manner [42]. The positively charged calcium ions compressed the diffuse layer of the electric double layer of impurities present in water, weakening the repulsion between impurities and facilitating better coagulation process. Apart from increasing the yield (number of compounds with coagulation capability) of extraction, the purity of the natural coagulants can also be enhanced to decrease the coagulant dosage and the impurities. The organic compounds in the natural coagulants that do not take part in coagulation procedure will possibly end up in the treated water as dissolved organic matter [44]. The presence of these organic residues is discarded as it will cause bacteria regrowth in the water and serve as substrate for the formation of hazardous disinfection by-products [45, 46]. Hereafter, the extracted natural coagulants must be purified to avoid such undesirable effects from using natural coagulants. The first step of purification is removing the oil content in the natural coagulant extract through the use of appropriate solvents such as ethanol and hexane [27, 41]. Hoa and Hue [27] have shown that purification with n-hexane solution managed to decrease the lipid content of Moringa oleifera seed extract down from 35% to 2% [27]. The reduction in lipid content improved COD removal and the turbidity efficiencies of the purified natural coagulant since the oil component did not benefit in coagulation procedure and would, on the other hand, add to the impurities in the water. After the removal of oil content, the natural coagulant extract can be further purified to get final product concentrated with active coagulation compounds via various purification procedures such as ion exchange, ultrafiltration, lyophilization, dialysis, chemical precipitation [29, 44, 47-49]. Sánchez-Martín, Ghebremichael [44] investigated the effect of purification extent (ion exchange chromatography using NaCl solution) on the coagulation performance of Moringa extract [44]. It was discovered that the optimum dosage of the single step purified (elution with 0.6 M NaCl) coagulant was two times higher than the two-step purified (first elution with 0.3 M NaCl followed by second elution with 0.6 M NaCl) coagulant in terms of turbidity removal. It was assumed that during the first elution, proteins without coagulation capability were removed. This led to the production of more purified coagulant containing active coagulant proteins after the second elution. Fascinatingly, the purified coagulant by ion exchange procedure performed at par with the conventional alum coagulant in terms of dosage required (1 mg/L) and turbidity removal efficiency (83%) for natural river water [29]. Without further purification, the Moringa extract could only achieve 50% removal of turbidity at the similar dosage or required four times higher dosage for removal efficiency of 83%. This showed that purification procedure can produce natural coagulant with higher proportion of active coagulation compounds, which subsequently leads to better performance even at lower optimal dosage. Due to the high cost associated with ion exchange chromatography, researchers have sought another purification approaches that are more economically viable at industrial level. A relatively simple chemical precipitation (using ammonium sulphate) of compounds possessing coagulation activity have been proposed for the purification of Moringa extract [48, 49]. Choudhary and Neogi [49] reported that the natural Moringa extract isolated using 30-60% and 60-80% saturated ammonium sulphate exhibited superior turbidity removal efficiency with a slightly better performance as compared to alum [49]. In addition, the purified natural coagulant did not affect nor change the pH of the treated water, an observation that alum coagulant failed to uphold since it reduced the pH to acidic condition. Later, the presence of a simple and effective isolation and purification method for natural Moringa extract might potentially help to yield natural coagulant with great coagulation activity. Likewise, extraction conditions such as acidity, temperature, and solvent will affect the yield of the compounds responsible for coagulation from the natural sources (e.g. garden cress, Basil seeds, and cactus) [34, 50, 51]. Generally, these compounds are originated from the polysaccharides that normally form the plant cell wall or are present in the form of mucilage. To release the polysaccharides during the extraction process, the plant cell wall has to be broken. Extraction conducted at high temperature may promote the solubilization of the compounds that are holding the polysaccharides and increase the yield [50, 51]. Though, the temperature must be controlled at the optimal level, otherwise extreme heat might finish the polysaccharides present in the natural coagulant and subsequently decrease the mucilage yield. An acidic extraction environment may also facilitate the breakdown of cell wall and release the coagulating compounds [52]. The use of appropriate solvent such as acetone can enhance the extraction efficiency of mucilage and enable the extraction yield in larger quantity be carried out with minimal amount of solvent used [50, 53]. Judging from the variance of extraction conditions, investigation on the influence of these factors should be conducted to ensure the maximum extraction of active coagulation compounds from the natural sources. The extraction and purification procedures of natural coagulants from other plant sources (e.g. Ocimum basilicum, Phaseolus vulgaris, seeds of Plantago, chestnut, Quercus robur, and cactus pads or Hibiscus from Opuntia species) are almost alike with the procedures involved in the production of Moringa coagulant [17, 35, 36, 54-58]. Overall, the extraction and purification of all plant based natural coagulants (including Moringa) are based on three steps, as shown in Fig. 4 [26].

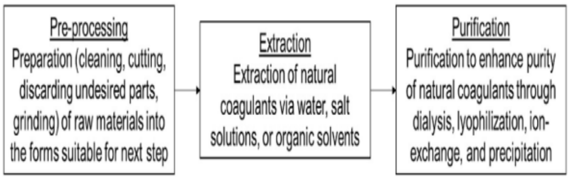

Fig. 4. General processing steps in the production of natural coagulant from plant-based sources [26]

The first step involves preprocessing of the sample where it is cleaned and converted into the form (normally in fine powder) appropriate for second stage. In the second step, the mixtures possessing coagulation activity are extracted using salt solution, water or appropriate solvent. The third step is the purification where only the compounds indeed contributing to coagulation procedure are purified. Nevertheless, of the plant, the compounds contributing to coagulation activity are either protein present in the extract or polysaccharide. The coagulation performance efficiency depends on the purity of the active compounds. Though, the scope of study for the natural coagulant stated above is not as intensive and thorough as compared to Moringa coagulant. The effect of the extraction and purification aspects on the coagulation performance for those natural coagulants is not covered in depth. Indeed, extracts taken from several numbers of natural plants reportedly possess coagulation capability, as reported in the precedent literature reviews [1, 21, 23]. Most of these studies stopped at showing the coagulation capability, and advance pursuit for optimization and in-depth understanding on the natural coagulants has been limited. Having said that, to promote the extensive use of natural coagulant, intensive study on the exploration of appropriate method of extraction and purification of the crude extract is required to remove the non-active components and to know the nature and characteristics of the active component in the natural coagulants. In comparison to natural coagulant from plant-based resources, chitosan is commercially extracted from crustacean shells (krill, crab, crayfish, and shrimp [59]. To separate chitin (chitosan is deacetylated derivative of chitin) from crustacean shells, chemical processing stages such as deproteinization (with sodium hydroxide) and demineralization (with hydrochloric acid) are usually applied to remove proteins and calcium carbonate (the main components of shells), respectively [60]. However, these processes normally take a long time and require high operating temperature which might reduce the quality of the chitosan. Also, chemical processing stages cause secondary waste from the excessive usage of alkali and acid solutions [13]. Physical auxiliary approaches (such as microwave radiation, irradiation, ultrasound, compressional puffing-pretreatment, and freezing/thawing) have been proposed to minimize the opposing impacts of chemical processing stages while at the same time improving the quality and purity of extracted chitosan [61-65]. For instance, ultrasound applied to the solution during demineralization increased the connection between acid and crustacean shells, helping to reduce the extraction time and produce less crystalline chitin for better conversion to chitosan [65]. Microwave radiation on the other hand accelerated the reaction time during deproteinization which could potentially cut down the extraction cost of chitosan[63]. However, the proposed auxiliary approaches exhibited advantages including simplicity environmentally friendly, and improvement of product quality, the large-scale extraction remains as chemical processing since it is less complicated and has been well-established. Hence, further upscaling study on the costing associated with auxiliary methods should be conducted to verify the benefits of advanced extraction and purification of chitosan from crustacean shells.

3.3. Hybridization with inorganic or other types of coagulants

As previously mentioned, under certain conditions, natural coagulants may not be as useful as compared to conventional inorganic coagulants. Though, the environmental benefits of natural coagulants could not be avoided. To harness the benefits of natural coagulants without sacrificing the treatment efficiency, apart from the chemical modification discussed in the previous section, the natural coagulants could be used together or mixed with other types of coagulants (normally inorganic types). This strategy can be accomplished in two ways: dual coagulant or composite coagulant and coagulant aid [20, 23, 66]. The former is produced by combining two types of coagulants as a single working composite coagulant, while coagulant aid is the materials used as an auxiliary to the primary coagulant (adding some time after the dosing of primary coagulant). Hybridization between non-natural coagulants or synthetic have been extensively reported but the focus in this section is the hybridization that involves the use of natural materials [67]. Ma, Hu [68] prepared a composite coagulant comprised chitosan and aluminum chloride by mixing the two coagulants together in solution[68]. The composite coagulant outperformed the individual coagulation process by achieving the optimal removal efficiency of M. aeruginosa (a harmful cyanobacterium that can produce toxins that adversely affect aquatic ecosystems and human) with lower dosage. It was reported that the polymer chains of chitosan and the steric crowding of aluminum hydroxide precipitates gave rise to entrapment and bridging mechanisms for the removal of M. aeruginosa. Both the components of the composite coagulant exerted little and probably no stress on the cells, indicating that negligible of cell damage occurred during the coagulation process. In addition, the composite coagulant could effectively remove extracellular organic matter. This was beneficial as it indicates that the risk of disinfection by-products formation during subsequent disinfection process would also be lessened. Overall, the combination of natural coagulant (chitosan) with the conventional coagulant (aluminum chloride) has proven to be an effective treatment process for the removal of harmful cyanobacteria which is normally found in highly eutrophic (polluted) water. Apart from being mixed into composite coagulant, the popular natural coagulant - chitosan - has also been used as coagulant aid for wastewater treatment. The use of chitosan as coagulant aid to aluminum-based primary coagulant has enhanced the removal efficiency of dye pollutants by 5-60%, especially at lower dosage of aluminum coagulant [69]. This could be attributed to the strong interaction between chitosan and aluminum-dye aggregates. The long chain structure of chitosan with abundance of amino groups could interact with the aluminum aggregates through charge neutralization mechanism, which would bind the small aggregates to form larger flocs. The bridging between the flocs via chitosan would increase the flocs size and strength, the characteristics desired for effective coagulation and sedimentation processes. Alum, being one of the most widely used inorganic coagulants in water and wastewater treatment, has been a concern for public as it is tied to the dispute of whether or not it causes Alzheimer disease. Natural coagulant aid can be used to reduce the consumption of alum coagulant as part of the effort to phase out the use of alum in the future. Natural seed gum extracted from Cassia obtusifolia seeds has shown promising potential as a coagulant aid to cut down the consumption of alum in the treatment of palm oil mill effluent, an abundant agricultural effluent discharged from the oil palm extraction mills. Shak and Wu [70] reported that the amount of alum used for optimal treatment efficiency has been cut down by 55% (2.57 g/L to 1.15 g/L) with the inclusion of natural seed gum as coagulant aid [70]. Owing to the high molecular weight and polymeric structure of natural seed gum, more impurities would be adsorbed onto the coagulant aid while at the same time the formation of larger aggregates would be promoted through bridging mechanism. These characteristics have made it possible to compensate for the reduction of alum consumption. The combined treatment revealed that the use of natural coagulant aid could significantly reduce the consumption of chemical coagulants and similar trend should be explored for other types of water sources. Study conducted by Wu, Wang [71] had shown the benefits of having coagulant aid (sodium alginate) for the treatment of dying wastewater (synthetic and real) with alum as the primary coagulant [71]. Their findings showed that not only had the addition of sodium alginate as coagulant aid improved the overall colour removal efficiency, but the synergistic improvement (with 1 ppm of sodium alginate) decreased the dosage of alum (4.5 ppm) required for the same treatment efficiency when alum (6 ppm) was used alone. The reduction of alum consumption could potentially cut down the costs (coagulant and sludge handling) and minimize the environmental impacts arising from alum coagulant. The bridging ability of sodium alginate reportedly facilitated the formation of larger flocs with greater resistance to breakage. This indicated that with the addition of coagulant aid, the flocs would settle down quicker than the smaller flocs formed when alum was used alone. The short retention time coupled with larger floc size can lead to footprint reduction of coagulation-sedimentation units (more compact). Treatment with real dying wastewater also observed 5-10% improvement in colour removal efficiency when sodium alginate was used as coagulant aid to alum as primary coagulant. In another study conducted by Wang, Hou [72] sodium alginate was coupled with polyaluminum chloride for the removal of copper oxide nanoparticles and humic acid [73]. The impacts of the presence of sodium alginate as coagulant aid on the removal efficiency and subsequent ultrafiltration membrane performance were evaluated. Commonly, the extra of coagulant aid improved the contaminants removal efficiency up to 20-30% while a little minimizing the membrane flux decline. The initial coagulation process involved the formation of aggregation between the positively charged aluminum coagulant and negatively charged copper oxide and humic acid contaminants. These micro flocs will then be bridged with the alginate polymers through the carboxyl functional groups to form "egg-box" structures. These gel networks would then sweep across the solution to entrap remaining contaminants, which explained the improved removal efficiency when coagulant aid was present. At the same time, the addition of sodium alginate enlarged the floc size and minimized the blocking of membrane pores by small particles. This showed that natural coagulant aid can perform well in enhancing the coagulation performance while at the same time benefiting the downstream treatment process. Though Moringa-based coagulant is as popular as chitosan with numerous publications citing the usefulness as natural coagulant in water and wastewater treatment, its hybridization use with other types of coagulants has not been widely reported. From the few articles relevant to this topic, Moringa-based coagulants can be used together with aluminum sulphate in both ways, either mixed together or dose prior or after the dosing of alum. Ghebremichael, Abaliwano [74] reported that dosing the natural coagulant prior alum would result in better removal of turbidity (20% increment) and dissolved organic carbon [74]. Exposing the Moringa coagulant to high turbidity water would facilitate the formation of micro-flocs, which would then be entrapped and adsorbed easily to the aluminum hydroxide precipitates. Furthermore, the use of natural coagulant aids reduced the alum dosage by about 50-75%. Similar benefits (higher turbidity removal and reduced alum consumption) can also been achieved by dosing both alum and Moringa coagulants together [75]. In contrast, Freitas, de Santana [76] highlighted that dosing the Moringa coagulant after alum would result in better turbidity reduction capacity compared to dosing both together [76]. It was postulated that when both were dosed together, the natural coagulant would interact with both suspended particles and aluminium ions. This reduced the available aluminium ions for the formation and removal of suspended particles. On the other hand, dosing the Moringa coagulant after alum would not disrupt the coagulation activity by alum. Instead, the natural coagulant helped to promote the formation of larger flocs for removal and at the same time reduce the amount of aluminium residue in the treated water (0.3 mg/L as compared to 35.5 mg/L using alum only). This demonstrates that the dosing sequence and hybridization mode for the incorporation of natural coagulants with conventional coagulants have to be designed properly as the combination may perform differently according to the type of water sources. Alternative to chemical-dosing coagulation process is the electrocoagulation that generates coagulating compounds from oxidation of metallic electrodes. Electrocoagulation has also been studied extensively for the treatment of various wastewater and it shares the same concern as chemical coagulation process highly reliant on ferric and aluminum-based electrodes that form hydroxides for the removal of impurities in water sources. The sludge produced and the excessive coagulants in the treated water will then become an issue for the plant operators due to the presence of metallic compounds. Hence, to decrease the consumption and production of excessive coagulating compounds, natural coagulant aid can also be applied to help the operation of electrocoagulation procedure. Adjeroud, Dahmoune [77] evaluated the performance of electrocoagulation process with and without the presence of cactus juice (coagulant aid) for the removal of turbidity in synthetic wastewater [77]. It was found that the cactus juice significantly improved the turbidity removal by 15% as compared to 72% of removal efficiency without the coagulant aid. The improvement was made possible through adsorption mechanism where the charged sugars content in cactus juice could potentially interact with cations (coagulants from electrodes) that were binding the suspended particles in the solution.

4. Sustainability of natural coagulants

Although performance efficiency is one of the most important factors being emphasized in water and wastewater treatment processes, other criteria answering the long-term reliability of the technologies are equally important, especially with the call for sustainable development by the United Nations. In general, sustainable development can be defined as "the development that meets the needs of the present without comprising the ability of future generations to meet their own needs" [78]. In the context of water and wastewater treatment processes, the sustainability can be considered from the integration of environmental, social, economic, and technical aspects [79]. Meanwhile the focus of this literature review is on natural coagulants and its performance in wastewater and water treatment, the sustainability criteria have been adjusted from past literature to meet the objective of this review (as shown in Fig. 3).

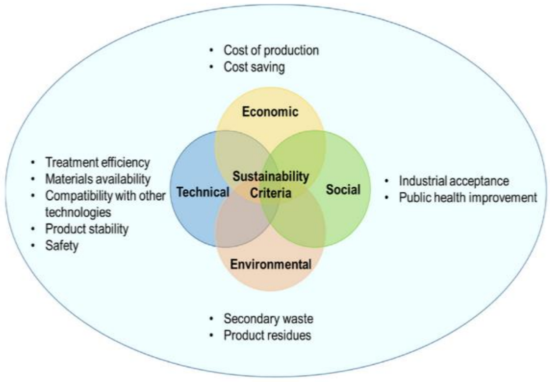

Fig. 5. Sustainability criteria commonly considered for water and wastewater treatment process [79].

5. Challenges of acceptance of natural coagulants

5.1. Practicality and feasibility of real application

Most of the reported performance results of natural coagulants have been limited to lab-scale studies and the transition to field tests and real industrial applications has been limited. The competence of natural coagulants in bracing the real application challenges such as steady supply of natural coagulants with consistent quality, fluctuating feed water quality, and storage and handling of natural coagulants has not been confirmed. To what extent the advantages of using natural coagulants over conventional coagulants in the real application has yet to be justified. The good ideas of natural coagulants enhancement such as integration with other treatment technologies, enhancement through chemical modification, multifunctionality, hybridization with other types of coagulants have been shown in many experimental studies. Nevertheless, the practicality of using these types of natural coagulants has not been well understood. The challenges of technical issues, mass-production, and toxicity of these coagulants coupled with the impacts on the other treatment procedures are the main concerns that require real application for the revelation of application feasibility of natural coagulants.

5.2. Sustainability of natural coagulants

As discussed earlier, the use of natural coagulants met few of the sustainability criteria and a few more aspects could not be verified due to the lack of data. The main concerns of technical criteria are the quality, stability, and safety aspects of natural coagulants, which will control the consistency of performance and feasibility of the coagulation process. The challenge lies in the continuous supply of sufficient amount of natural coagulants with desired properties without being affected by the various differences in the extraction and purification or synthesis of natural coagulants. From the environmental perspective, the secondary wastes after coagulation process and during the synthesis/extraction processes as well as the residual of natural coagulants in treated water could pose a safety challenge to the environment and consumers. For economic sustainability, the costs incurred or saved due to the use of natural coagulants have received some mixed opinions. Further detailed economic study is required to clarify the confusion arising from various speculations. In social sustainability, the low industry approval of natural coagulants could be attributed to the lack of real application of natural coagulants or pilot-scale and the lack of regulatory support from the government agency. On the other hand, the niche application of natural coagulants in rural areas or regions facing with economic water scarcity may be helpful in improving the living conditions of those people. Generally, justification and clarification of the above concerns could shed the light on the sustainability potential of using natural coagulants in wastewater and water treatment procedures.

6. Conclusion

Nature has gifted humans with solutions to obtain clean water and to remove the pollutants discharged into the water body from anthropogenic activities. The materials possessing coagulation capability can be obtained from various natural sources. It is therefore dependent on the wisdom of humanity uncover ways to fully utilize the natural materials for water and wastewater treatment purposes. Literature has demonstrated the capability of natural coagulants in removing impurities (especially suspended solids and colloidal particles) that cause problem for subsequent treatment procedure and health problems for consumers. Unfortunately, the extensive application of natural coagulants in water industry is still far from reality and the acceptance of natural coagulants over the conventional coagulants is still low. Thus, efforts in raising the confidence of water utility by showcasing the capability of natural coagulants should be highlighted. Among these are: the compatibility of natural coagulants with other treatment technologies in integrated/hybrid treatment process; the modification of natural coagulants for marked improvement in coagulation performance efficiency; the possibility of hybridizing natural coagulants with other types of coagulants; the improvement of extraction and purification approaches for high purity of natural coagulants; and the synthesis of multifunctional natural coagulants. Coupled with the sustainability evaluation of natural coagulants, the direction of future research for further improving the capability of natural coagulants and boosting the confident of industry players can be obtained.

7. References

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