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Review

Comprehensive Review of Modification, Optimisation, and Characterisation Methods Applied to Plant-Based Natural Coagulants (PBNCs) for Water and Wastewater Treatment

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Abstract: This review investigates the modification, optimisation, and characterisation of plant-based natural coagulants applied to water treatment. The disadvantages of plant-based materials hinder their application as alternatives to chemical coagulants, necessitating their modification to alter and enhance their physicochemical properties, making them suitable for application. Modification via microwave-assisted grafting copolymerisation has been found to be the most preferred approach compared to conventional methods. Optimisation of the coagulation process using response surface methodology has been shown to be practical. Different techniques are used in determining the physicochemical properties of plant-based natural coagulants. Some of these techniques have been tabulated, describing the properties each technique is capable of investigating. In conclusion, modification and optimisation of plant-based natural coagulants will result in the production of new materials that are stable and suitable for application as coagulants in water treatment.

Keywords: coagulation; characterisation; modification; optimisation; water and wastewater treatment

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1. Introduction

The role of water in life is evident [1–4]. Water is a transportation medium in the human body that assists in flushing waste from the body. It keeps the body hydrated, which is necessary for survival. Moreover, the economic role that water plays in the world cannot be overemphasised. According to Water.org [5], the annual economic benefit of universal access to basic water and sanitation has been valued at USD 18.5 billion from avoided death only. In the statistics, for every USD 1 spent on supplying clean water and sanitation, around USD 4 economic return is gained from low health costs, thus increasing productivity and decreasing early death in children. This makes drinking water treatment a significant aspect of any nation's economy.

In water treatment, the coagulation and flocculation process, in which suspended and colloidal particles agglomerate to form flocs heavy enough to quickly settle to the bottom of the clarifier, is essential. This process produces a supernatant, free from visible particles and ready for filtration [6]. However, there is more to drinking water coagulation and flocculation processes than floc formation and settling time [7]. The use of chemical coagulants has been shown to leave trace amounts of chemicals in water filtrate, which has been associated with neurodegenerative diseases due to long-term ingestion of these traces of chemicals. This negates the essence of water treatment; hence, an alternative to using these chemicals is necessary [8,9].

Due to the health and environmental problems caused by these chemical coagulants, the search for alternative coagulants that are non-toxic and environmentally friendly has been and is still a popular topic for researchers in the water industry. These potential alternatives, referred to as natural coagulants, are broadly classified into plant-based and non-plant-based natural coagulants. Plant-based options are more investigated because of their availability and biological formations. This paper reviews the modification, optimisation, and characterisation methods used to enhance plant-based natural coagulants for water treatment.

2. Literature Review

2.1. Plant-Based Natural Coagulants (PBNCs)

The conventional coagulants used in water treatment are chemical-based coagulants (CBCs). The most common CBCs are alum salts and ferrous salts, and the significant advantages of their usage are their suitability and low cost [6]. There is no doubt these CBCs have high efficiency in treating water; however, their resulting health and environmental problems are the reason why an alternative to their use is necessary. Plant-based natural coagulants (PBNCs) have been shown to be a promising alternative. The active agents, mainly extracted as polysaccharides, have demonstrated remarkable performance as natural coagulants in water and wastewater treatment [10–12]. Plant-based natural coagulants' advantages include excellent biodegradability, biocompatibility, sustainable production, low cost, and high availability [8,13–20].

Plant-based natural coagulants are naturally occurring macromolecules of carbohydrates extracted from plant fruits, leaves, seeds, peels, etc. [21,22]. They contain some physicochemical properties proposed to be responsible for the flocculation process in water treatment. Among these properties are various functional groups, including carboxyl, hydroxyl, and phenolic [21,23]. However, there are disadvantages associated with these plant polysaccharides, including thermo-sensitivity, pH sensitivity, sensitivity to severe conditions, the possibility of microbial contamination, and loss of viscosity during storage [13,24–26]). Furthermore, some plant-based natural coagulants are anionic, making them more suitable as coagulant aids in water treatment [27,28]. These and other problems associated with using PBNC have hindered the progression of their practical applications and commercialisation. However, several modification methods have been employed to enhance the performance of various plant polysaccharides to overcome these disadvantages [10,29]. Figure 1 presents a flow chart showing stages for investigating PBNCs' potentiality as natural coagulants.

2.2. Modification of Plant-Based Natural Coagulants Using Grafting Copolymerisation Method

Plant-based materials and their recent progression are fascinating areas of applied polymer science that is gaining recognition [30,31]. Their emergence towards replacing synthetic materials is becoming research niche. Researchers mainly focus on the total replacement of synthetic materials with natural materials, or modifications to reduce the content of the synthetic materials or even modification using two raw materials. Modifying the properties of a polymer to meet its required specifications for application is essential [32–35]. There are several ways of modifying polymer properties, including blending, curing, and grafting. Grafting is a method where covalent bonding of a substance onto a polymer chain occurs.

In simple terms, the effective way is to mixing two or more different types of polymers to form a copolymer with enhanced characteristics [29,32]. Grafting-from, grafting-to, and grafting-through are controlled copolymerisation processes in preparing well-defined copolymers. In grafting-from, growth of the copolymer chain occurs in situ from an initiator that has been previously hooked to a monomer's surface. Grafting-to or grafting-on, which arose from the development of "click" chemistry, involve the individual synthetisation of two or more different monomers, and then connecting them, where the end functionalised polymer reacts with reactive sites on the monomer's surface. For grafting-through, polymerisable groups are hooked onto the surface of monomers [10,36–39].

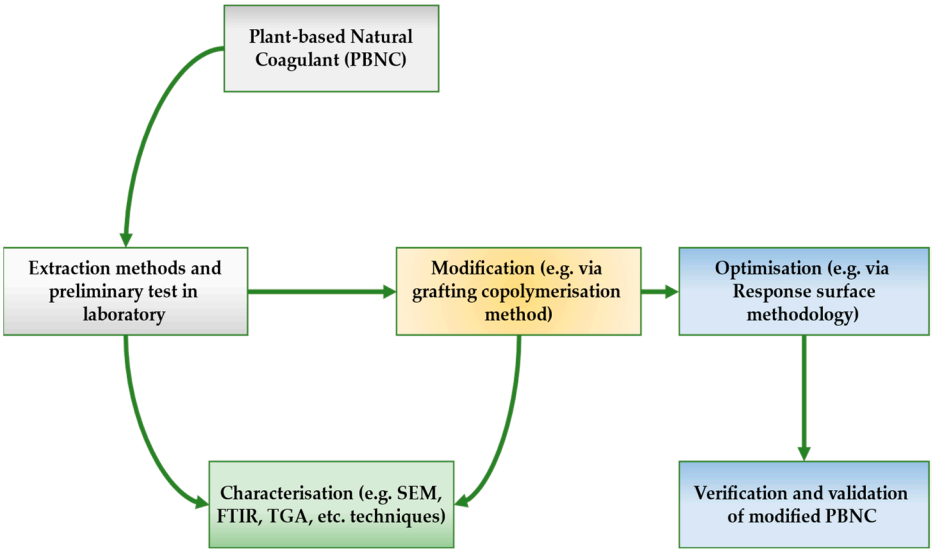

Figure 1. Stages for investigating the potentiality of natural coagulants. The first horizontal arrow from the extraction chart is the characterisation of material before modification, and the second horizontal arrow from the modification chart is the characterisation after modification.

Natural plant polysaccharides are mostly unsuitable because of their poor stability and substantial swelling in the natural environment. Their modification through graft copolymerisation to enhance their characteristics is necessary to make them attractive natural materials and increase their resilience and suitability in the biological environment [24,26,29]. Graft copolymerisation research is a priority of polymeric research because it enhances modify biopolymers' characteristics to obtain an upgraded natural material with enhanced properties [10,24,25,29,40]. Furthermore, it is important to understand the difference between copolymers. Copolymers are classified into block copolymers, random copolymers, alternate copolymers, and graft copolymers. In brief, a block copolymer consists of a combination of two or more segments of different polymers linearly joined from end-to-end. A random copolymer is when a monomer is attached randomly to the polymerised polymer, and an alternate copolymer has its monomer present in an ordered manner. A graft copolymer involves the mixing of a natural polymer and a synthetic polymer. In this case, the natural polymer is mostly the backbone of the grafted polymer, with the synthetic monomer as the side chains attached to the new polymer product at multiple sites [10].

Recently, natural plant polysaccharide modifications through graft copolymerisation procedures concerning different approaches have been studied. Several vinyl monomers, such as acrylamide (AM), methacrylamide (MA), methyl methacrylate (MMA), N-acrylonitrile, tert-butyl acrylamide, N-poly vinylpyrrolidone (NPVP), and 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC), have been grafted to many plant-derived polysaccharides to optimise the potential properties [29,41]. The structural features of plant polysaccharides, the type and characteristics of the grafting monomers, grafting efficiency, and grafting ratio, are all factors that determine the characteristics and features of the grafted copolymer. Plant

polysaccharides-g-copolymers have been used in several fields and industries, including civil engineering, biomaterials, agriculture, wastewater treatment, food, cosmetics, and pharmaceutical industries [23,29,37,42,43].

Among the methods of graft copolymerisation is conventional radical grafting copolymerisation, where, generally, hydroxyl (- OH) groups of polymers are involved. This occurs through radical polymerisation reaction under the influence of redox and thermal initiators [24,29]. Some examples of different polysaccharide-grafted copolymers synthesised by different redox initiators, as outlined by Nayak, et al. [29], include guar gum (GG) with an initiation system of H_2O_2, and cerium ammonium nitrate (CAN) to produce new polysaccharide copolymers GG-g-PMMA and GG-g-PAN, respectively; gum acacia (GA) with an initiation system of potassium persulfate, and CAN to produce GA-g-PAM and GA-g-PMMA, respectively; tamarind kernel polysaccharide (TKP) with CAN to produce TKP-g-PAM, etc. Another graft copolymerisation method is macromonomer radical grafting copolymerisation. Polymers of lower reactivity are chemically modified to form monomer-like structures as grafted copolymers. In most free radical grafting reactions, vinyl-functionalised polymers are considered macromonomers since these involve several active vinyl groups. Hence, synthesising many macromonomers is the main issue influencing the grafting reaction and grafted copolymer product quality, as shown in Nayak, et al. [29]. In addition to the high cost of conventional grafting copolymerisation, this method has difficulties treating solid samples, and undesirable chemicals are often produced because of the system's dependence on different chemical initiators. The production of these chemicals may affect the safety application of grafted copolymers in many areas of application. These issues led to the emergence of high-energy initiated grafting copolymerisation. The simplicity of high-energy initiated grafting copolymerisation and its advantages concerning its grafting capabilities in soluble and non-soluble samples make it a preferred method for grafting different polysaccharides [10,29,42].

High-energy-initiated grafting copolymerisation is subdivided into four methods as outlined by Setia [10] and Nayak et al. [29]: microwave-assisted, gamma radiation-initiated, ultraviolet radiation-initiated, and electron beam-initiated grafting copolymerisation methods. Grafting by radiation has several advantages over the conventional grafting method. The radiation-induced method is regarded as the most convenient method of grafting copolymers. It is easily controlled due to the small number and length of copolymers. It does not change the molecular weight of the copolymer, and chains attached to the backbone can be achieved at different depths as the penetrating power of the radiation is regulated [44–46]. Other graft copolymerisation methods include click chemistry and atom transfer radical grafting copolymerisation. A flowchart outlining grafting copolymerisation methods is shown in Figure 2.

Microwave Radiation-Induced Graft Copolymerisation

Microwave radiation is an effective method for the grafting copolymerisation process. In microwave-assisted copolymerisation, there is high grafting efficiency and a high yield of polysaccharide copolymers. The processing time is relatively short, with lower or no addition of initiators. Generally, the grafting extent can be adjusted using the microwave irradiation parameters controller (which controls time and radiation strength). Primary radicals are generated more productively. These advantages may be due to the electromagnetic radiation of 300 MHz—300 GHz frequency generated during the irradiation, which is directly exposed to the mixture [10]. The radiation separates polar bonds, producing free radical sites on the polymer's backbone. However, the nonpolar part of the polymer backbone remains intact. In microwave-assisted graft copolymerisation, the separation of -OH creates a free radical site on the polymeric backbone, which can react with vinyl monomers leading to the expansion of the polymeric chains [29,47–50].

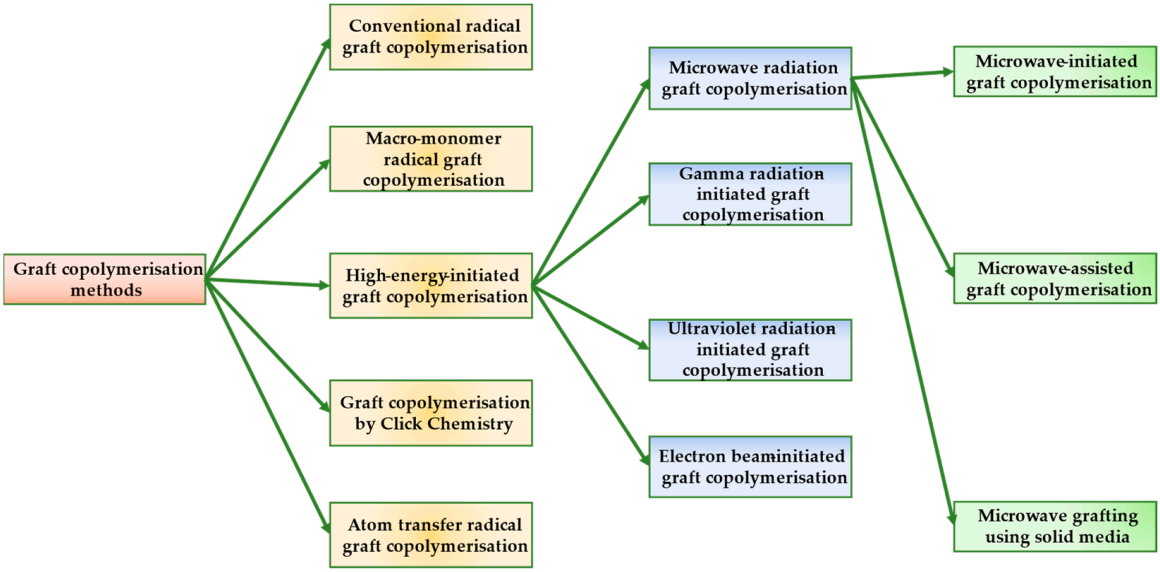

Figure 2. Different methods of grafting copolymerisation with a focus on high-energy initiated methods, within which microwave-assisted grafting has shown to be the most preferred.

Microwave-irradiated grafting has three types: (1) microwave-initiated grafting, (2) microwave-assisted grafting, and (3) microwave grafting using solid media [10,47,51]. For microwave-assisted grafting, redox initiators are used. Along with microwave irradiations, radicals are produced in the presence of redox initiators, which play an important role in converting microwave radiation into heat energy. Heat generation is responsible for the free radical generation and successful production of grafted copolymers. One clear advantage of the initiator is that it produces an efficient free radical in a short period of microwave power. Furthermore, the grafting efficiency has been shown to be increased to a certain level [10]. A recent example is the graft copolymerisation of 2-methacryloyloxyethyl trimethylammonium chloride (DMC) on lentil extract (LE), producing LE-g-DMC, a natural coagulant with high water-treatment efficiency and being 75% more efficient than alum [41]. Microwave-assisted grafting has been shown to be more efficient than the conventional radical graft copolymerisation method [52].

Research on the microwave-assisted grafting method has been conducted in different fields. In a recent pharmaceutical example, Bal and Swain [53] conducted a microwave-assisted synthesis of a polyacrylamide-grafted polymeric blend of fenugreek seed mucilage-Polyvinyl alcohol (FSM-PVA-g-PAM), and its characterisations as a tissue-engineered scaffold and as a drug-delivery device. FSM-PVA was grafted with acrylamide (AM) and ammonium persulfate (APS) as initiators. The best grade based on grafting efficiency was attained using varying amounts of AM and APS. After the grafting process, Fourier transform infrared spectroscopy (FTIR), ^{13}CNMR spectra, X-ray diffraction, elemental analysis, thermogravimetric analysis, and scanning electron microscopy (SEM) were used to investigate the new product. The intrinsic viscosity measurement showed that the new product has a longer chain length than the native material, exhibiting more swelling tendencies. The new product was also found to be more stable, and more amorphous properties were found compared to the original material under thermal and X-ray analysis. FTIR and NMR indicated the presence of amide and hydroxyl groups confirming the grafting process. When used in animals, the SEM image of the new product showed its biodegradability and biocompatibility, and the product was found to be suitable for tissue-engineered scaffolds. Other research in controlled drug delivery, enhanced drug delivery, targeted drug delivery, etc., has been performed, and grafted copolymers have been shown to be promising in achieving the research objectives [10,29].

Graft copolymerisation of polysaccharides for potential application to solve environmental issues is promising. Microwave-assisted grafting is a popular method of improving

the properties of polysaccharides using domestic microwaves [10,29,41,53]. Though grafting is more than half a century old, its commercialised application is rare or non-existent. Its practicality will be essential, particularly in the water industry. Environmentally friendly coagulants/flocculants are necessary to eliminate chemical-based agents' usage, sustain a healthy environment, and provide safe drinking water free from trace chemicals. Table 1 outlines the study of grafted plant-based polysaccharides (PBNCs), via the microwave-assisted method, used as coagulants and flocculants in water and wastewater treatment, with their graft chain and initiation systems.

Table 1. PBNC-g-copolymers via microwave-assisted method, their graft chain, initiation systems, and usage as flocculants in water and wastewater treatment.

PBNC	Graft Chain	Initiation System	PBNC-G-Copolymer	Effluent Treated	Reference
Lentil waste extract (LE)	DMC (2-methacryloyloxyethyl trimethyl ammonium chloride)	CAN (Cerium Ammonium nitrate)	LE-g-DMC	Synthetic and Agricultural Wastewater	[23,41]
Sodium alginate (SA)	DMDAAC (Dimethyl diallyl ammonium chloride)	$(NH_4)_2S_2O_8$ + $NaHSO_3$ (Ammonium persulfate and sodium hydrogen sulphite)	SAD	Dye wastewater	[54]
Inulin (In)	PAM (Polyacrylamide)	CAN	In-g-PAM	Coal washery effluents	[55]
Agar (Ag)	P(HEMA) poly(2-hydroxyethyl methacrylate)	CAN	Ag-g-P(HEMA)	Wastewater	[56]
Sodium alginate (SAG)	PMMA (Polymethyl methacrylate)	CAN	SAG-g-PMMA	Coal fine suspension	[57]
Gum Ghatti (GGt)	PAM (Polyacrylamide)	CAN	GGt-g-PAM	Synthetic and municipal wastewater	[58]
Agar (Ag)	PAM (Polyacrylamide)	CAN	Ag-g-PAM	Synthetic wastewater	[52]
Carboxymethyl guar gum (CMG)	PAM (Polyacrylamide)	Potassium persulphate	CMG-g-PAM	Synthetic wastewater	[59]
Dextrin (Dxt)	PAM (Polyacrylamide)	Potassium persulphate	Dxt-g-PAM	Synthetic wastewater	[60]
Maize Starch (St)	PAM (Polyacrylamide)	CAN	St-g-PAM	Synthetic wastewater	[61]

2.3. Optimisation of Plant-Based Natural Coagulants Using Response Surface Methodology (RSM)

When experimenting, independent variables determine what happens to the outcome in focus [62]. One variable is often considered at a time, which often gives a poor result. However, it is not easy to simultaneously consider more than one independent variable [63,64]. This requires the application of statistical tools that are able to analyse the performance of different variables at the same time. Response surface methodology (RSM) is one of these statistical tools primarily used in the optimisation process that helps identify interrelationships between variables [65]. It assists in determining the best design of an experiment that will enable the identification of the said relationship between the variables [66,67]. It is a combination of statistical and mathematical techniques used to

construct models that assists in assessing the effect of several independent variables and obtaining their optimum values [62,68–70].

Carley et al. [71] further explained that RSM applications are primarily used in situations where several input variables determine the measurement and characteristics of a given process. Such performance measures are called responses, while the input variables are called factors, independent variables, or operating parameters [65,70]. These factors are under the researcher's control. Response surface methodology (RSM) further involves an experimental strategy for exploring the space of the process factors. Empirical statistical modelling has been developed to design an approximate relationship between the yield and the factors. RSM optimises methods for predicting and evaluating the values of the process factors that produce optimum values of the responses [62,71]. Results from the analysis are graphically described in a 3D plot or 2D linear graph. The RSM procedure consists of several stages (depending on the application), including factor selection, design of experiment (DOE), laboratory experiment based on DOE, model selection, checking model adequacy, graphical presentation of model, and, finally, optimisation [62,68,71,72].

The first stage of any experimental design is identifying and selecting influential factors. Sometimes this is conducted by an assumption of one factor at a time or by two factorial-level methods. Numerous factors may affect the response of a particular system under study. It is impractical to identify and control each small contributing factor. Therefore, factors with significant impact must be selected. A preliminary screening design may be an option to determine factors with a significant effect on the response. This leads to the design of experiment (DOE) [62,72].

Optimisation can be performed using different experimental designs, and the differences between these designs are based on the experimental points chosen and the number of experiments to be run. These experimental designs include the Box–Behnken design (BBD) and central composite design (CCD). Generally regarded as a preliminary three-level design (3^k), Box–Behnken design is a spherical second-order design (rotatable or nearly rotatable). Industrial researchers use BBD more often than other design methods because of its economic properties. BBD requires only three levels for each factor where the settings are −1, 0, and +1. The number of experiments in BBD is $N = 2k(k-1) + C_o$ (where k is the number of factors and C_o is the number of central points) [62,68,73,74]. CCD, on the other hand, consists of first-order design factorial points (2^k), in addition to axial points (2 K) and centre points (n_o), which allows the determination of the parameter of the second-order model. The number of experiments in CCD is defined as $N = n_o + 2K + 2^k$ where K is the number of parameters and n_o is the number of centre points [62,75,76].

The next stage is to simulate the set of experiments designed in the laboratory. This step requires experience as it needs to be accurate to obtain good results. Depending on the field of research, the effect of physicochemical properties needs to be considered; thus, performing replicate runs is necessary even if this was not suggested by the design. The average results are calculated and used as the obtained results. Model selection is the next step, and deals with the mathematical model of the process. The models are generally polynomials with an unknown structure of the second-order quadratic formula. The quadratic formula describes the interaction between factors and evaluates critical points not exploited in the linear formula. The selected model is mostly improved using the correlation coefficient R^2 or by reducing the difference between $R^2_{predicted}$ and $R^2_{adjusted}$ to increase the model's accuracy. Achieving the latter requires the elimination of insignificant factors. After carefully selecting the model, the model adequacy needs to be checked, for which a graphical representation of the model is derived, which displays the performance of all factors with respect to the response. Then, the model can be optimised. Table 2 outlines some advantages and disadvantages of BBD and CCD as they are the designs that are most commonly used by researchers. Subsequently, Table 3 gives examples of water treatment processes optimised using response surface methodology.

Table 2. Advantages and disadvantages of BBD and CCD.

Design Type	Advantages	Disadvantages
Box–Behnken Design (BBD)	• BBD can be less expensive to implement than CCD with the same number of factors [77,78]. • BBD ensures that all design points fall within safe operating zones [77]. • BBD also ensures that all factors are not set at their high levels at the same time [77]. • BBD requires fewer experiments than CCD (e.g., 15 experiments are required for 3 factors compared to CCD with 20 experiments [78,79]. • BBD is easy to predict the lower and upper limits at 3 level points [80,81]	• If any runs are missing, the accuracy of the remaining runs in BBD may become critical to the dependability of the model [77].
Central Composite Design (CCD)	• CCD is robust in that even if runs are missed, it will not affect the accuracy of the model (i.e., CCD is insensitive to missing data) [82,83]. • CCD provides excellent prediction capability near the centre (bullseye) of the design space [82,83].	• CCD usually has axial points outside the "cube". These points may not be in the region of interest and may be impossible to conduct because they are beyond safe operating limits [83,84].

Table 3. Optimisation of coagulation and flocculation processes using response surface methodology along with optimum conditions of factors and responses considered.

Type of Process	Factors	Responses	Experimental Design	Optimum Conditions	References
Coagulation process of Agriculture wastewater using DMC grafted lentil extract (LE-g-DMC), and LE	pH, coagulants dosage, and settling time	Turbidity and COD removal	BBD	LE-g-DMC: pH of 6.7, a dosage of 63.08 mg/L and settling time of 5 min. LE: pH of 4, a dosage of 88.46 mg/L and settling time of 6.9 min	[23]
Coagulation process using red lentil extract (RLE)	pH, RLE dosage, and settling time	Turbidity removal	BBD	pH of 4, a dosage of 26.3 mg/L and a settling time of 2 min	[85]
Coagulation process using *Moringa Oleifera* seed extract (MOSE)	Settling time, agitation time, agitation speed, MOSE dosage	Turbidity removal	BBD	120 min of settling time, 10 min of 100 rpm agitation, at 3 g/L of MOSE	[86]
Coagulation process using Odaracha soil (OS)	pH, settling time, OS dosage	Turbidity removal	CCD	30 min of settling time, at 3 g/L OS and pH of 7	[87]
Coagulation process using *Moringa Oleifera* seed powder (MOSP)	pH, MSP dosage	Turbidity, colour, and COD removal	Random design load	pH of 7–9 at 0.1 g MSP	[88]
Coagulation process using (MOSP)	MOSP dosage, initial dye conc., pH, settling time, stirring speed and time.	Turbidity and dye removal	CCD	0.34 mg/L of MOSP, 7.88 mg/L dye concentration, pH of 6.93, settling time 113.15 min, stirring time of 13.52 min at 135 rpm.	[89]
Coagulation process using *Tympanotonos fuscatus* extract (TFC)	Dosage, time, temperature	Turbidity removal	BBD	Dosage of 1 g/L, for 16.5 min at 45 °C	[90]
Coagulation process using $FeCl_3$ and Sesbania seed gum (SSG) as aid	Coagulant dosage, and settling time	Turbidity removal	BBD	Coagulant dosage: $FeCl_3$ of 10.2 mg/L and SSG of 4.52 mg/L At a settling time of 2.5 min	[28]

Table 3. *Cont.*

Type of Process	Factors	Responses	Experimental Design	Optimum Conditions	References
Electrocoagulation process of Leachate	pH, Electrolyte dosage, electrode material, inter-electrode distance, current density, electrolysis time	COD removal	CCD	Electrode distance of 1.5 cm, with a current density of 50 A/cm^2, at electrolysis time of 240 min	[91]
Metal ion removal using red Algae	pH, initial ion conc., contact time, and biosorbent dosage	Pb(II) and Cu(II) removal	CCD	pH of 4.5, initial concentration of 40 mg/L, contact times of 115 and 45 min Pb(II) and Cu(II), respectively	[92]
Electrocoagulation for cationic dye	Electrolysis time, current density, pH, NaCl concentration	Dye removal and electrical energy consumption	CCD	Electrolysis time of 10 min, a current density of 80 A/m^2, initial pH 5, and NaCl concentration of 0.5 g/L	[93]
Coagulation process using Fe and Malva nut gum (MNG)	pH, and Fe: MNG dosage	Turbidity removal	FCCD	pH of 5.77, and Fe: MNG concentration of 0.05 mM:0.42 mg/L	[27]
Coagulation process using ferric chloride sludge (FCS)	Initial pH, FCS dosage, and initial dye conc.	Dye removal	CCD	pH of 3.5, FCS of 236.68 mg dried FCS/L, and initial dye concentration of 65.91 mg/L	[94]
Coagulation process using biocoagulants	pH, coagulant dosage, settling time	Turbidity removal	BBD	pH of 2–4, a dosage of 100–200 mg/L, and a settling time of 30 min	[95]
Coagulation process using poly-aluminium chloride (PACl) and alum	pH, and coagulants dosage	Turbidity and dissolved organic carbon	CCD	0.11 mM of PACl at a pH of 7.4 0.15 mM of alum at a pH of 6.6	[96]

2.4. Characterisation of Plant-Based Natural Coagulants Using Different Techniques

The physicochemical characterisation of materials is a vital study used in validating material properties. It offers knowledge of the materials' biological, chemical, and environmental effects and benefits. Furthermore, evaluating the physicochemical properties of a material is a fundamental analysis that can determine its applications [97].

There are different types of techniques used in the characterisation of materials. These include scanning electron microscopy (SEM), zeta potential, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-visible spectroscopy (UV-vis), UV-visible NIR (near infrared) spectroscopy, thermogravimetric analysis (TGA), atomic force microscopy (AFM), inductively coupled plasma mass spectrometry (ICP-MS), dynamic light scattering (DLS), Raman spectroscopy, and fluorescence spectrophotometry. Validating the properties of a material may require several of these instrument techniques because each instrument has its advantages and disadvantages.

Therefore, characterisation technique requirements are based on material type, properties, and intended applications [97–99]. An example of the characterisation techniques used can be found in Chua et al. [85], in which red lentil (*Lens culinaris*) extract was used as a novel natural coagulant for turbidity reduction. In their investigations, field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), zeta potential analysis, and energy-dispersive X-ray (EDX) analysis were conducted. FE-SEM revealed the irregular shape distribution structure of materials, and EDX analysis demonstrated the elemental compositions by weight (%) and atomic (%) of carbon (C), oxygen (O), potassium (K), phosphorus (P), calcium (Ca), etc. Elemental compositions determine macroscopic properties such as mechanic behaviours, including hardness, elas-

ticity, and weight; electrical properties (such as resistance); and chemical properties such as corrosivity resistance [100].

Zeta potential analysis determines the surface charge of the material, while FITR analysis identifies functional groups in materials [36]. Table 4 outlines the physicochemical characterisation of natural coagulants and grafted plant polysaccharides.

Table 4. Characterisation techniques used in investigating some native and grafted polysaccharides used as coagulants in water treatment.

Characterisation Techniques	Investigation	Reference
SEM	Surface, morphology, and particles distribution of the materials	[27,41,99,101–105]
FTIR	Functional groups properties of materials	[28,41,99,101–105]
XRD	coagulation and flocculation process	[101,102]
TGA	thermal stability of a material	[41,99,102,103,105]
Zeta Potential	Materials surface charge	[27,28,41]
EDX	Elemental composition	[28,41]
$^{13}C/H^{1}$ (NMR)	conformational and configurational changes in the material. It also determines the form and type of carbon and hydrogen atoms in a material.	[101,103,105]
UV-Vis	Optical properties of materials	[99,105]

The characterisation techniques are not limited to those presented in Table 4. The table shows a wide range of investigations conducted using the characterisation techniques to identify functional groups in materials, and to confirm the grafting process, percentage of grafting, and differences between native materials and their corresponding grafted copolymers. Characterisation of plant-based natural coagulants predicts treatment mechanisms and provides information on the modifications that are necessary for optimum application in water and wastewater treatment.

Furthermore, the investigation of flocs formed due to coagulation processes is as equally important as the characterisation of materials. The fragility and porosity of flocs formed during water treatment are evident in the coagulation process. Flocs are removed via the settling process, which is greatly affected by the properties of the flocs. Floc properties such as size, physical morphology, and compactness affect the settling process and the final process unit in water treatment, i.e., the filtration process. The flocs' properties significantly affect the system's treatment ability, and flocs' performances depend on the type of coagulant used [106–108].

The fragile nature of the floc can result in its breakage into smaller flocs due to some variable factors (e.g., turbulence, stirring pattern, and retention time); hence, it appears as a residual particle, rendering the coagulation process inefficient [109]. Therefore, a floc formed from the coagulation process and that settles easily is necessary for an efficient water treatment system. Thus, studying the floc properties developed using natural coagulants is inevitable to enable proper optimisation for an efficient water treatment system. The parameters investigated include floc distribution size, which is used in quantifying the extent of flocs in a system. This gives a good indication of how strong the flocs are. Jarvis et al. [110] observed that the flocs' strength increases with a decrease in their size. Floc formation is due to the balance between breakage and aggregation as flocs approach a steady-state size for a given shear rate. This steady-state floc size for a particular shear rate is a good indicator of floc strength. Various techniques have been developed to measure floc size; these include, but are not limited to, light scattering and transmission, microscopy, photography, video, and image analysis software.

Another parameter is the fractal nature of flocs, which relates to settling velocity. The fractal dimension gives an idea of flocs' irregularity and is used in estimating the compactness of flocs using 2D or 3D fractal dimension graphs. It is essential to investigate

and measure the compactness of flocs to know their strength and whether there is a need for optimisation for better settling and removal efficiency. It is worth noting that the final floc size distribution related to the system's hydraulic conditions is required when designing the mixing chamber for the coagulation process [111–113].

Zeta potential directly affects floc formation as it indicates the stability of colloids in suspension. If particle charge is dominantly positive or negative, the colloids tend to repel each other, preventing floc formation. Alternatively, if the zeta potential is low, the force of repulsion between particles is less. Therefore, the tendency for flocculation is high. Thus, the analysis of zeta potential is also an essential aspect of floc characterisation [6,109]. When the zeta potential is favourable for flocculation, charge neutralisation is the predominant mechanism. If the zeta potential of treated water indicates a low negative charge compared to the initial zeta potential, this shows the possibility of a charge neutralisation mechanism. On the contrary, if more negative zeta potential is observed, this indicates the possibility of adsorption, bridging, or sweep coagulation mechanisms.

After treatment, the leftover slurry due to the settled flocs, which are regarded as sludge, needs to be evaluated. Sludge evaluation is based on the compactness of flocs and the volume of sludge produced. The mechanisms of coagulation and flocculation, whether by charge neutralisation or interparticle bridging, etc., result in the compact nature of sludge and tend to give a sludge type its properties. The sludge volume index (SVI), measured in millilitres (mL) occupied by 1 g of sludge that has settled for 30 min, is an important measure. The index (a derived number) is used to describe the ability of the sludge to settle and compact [114].

Concisely, the characterisation of the sludge formed and its volume index contributes to determining the performance of plant-based natural coagulants and can suggest the need for the coagulants' optimisation.

2.5. Challenges and Future Perspectives of Plant-Based Natural Coagulants for Water and Wastewater Treatment

The use of plant-based natural coagulants (PBNCs) dates back to 2000 BC when plant materials were applied to clarifying drinking water [6,115]. Karnena and Saritha [116], in their brief timeline of PBNCs, outlined several historical applications for drinking water by rural dwellers, travellers, and even royalties. Similarly, today, PBNCs have been reported in some rural communities of Sudan, Tanzania, Mexico, and Peru [115–117]. Although the successful use of PBNCs was evident then, the quantity of water generally treated was small, and storage was only possible for a short period, as outlined by Ogden et al. [118]. An extended storage period is impossible due to the material's instability. Moreover, Alazaiza et al. [119] reported that during the coagulation process, rapid mixing could lead to the breakage of cells of coagulant materials, thus increasing the organic matter load, which may react with the disinfectant in the disinfection stage, thus producing by-products [120].

Another major challenge for PBNCs is the use of edible plants as coagulants. The challenge between meeting food demand and finding an alternative to chemical coagulants will undoubtedly hinder the progression of PBNCs to practical application. Furthermore, the current extraction methods of PBNCs are complex and sometimes uncertain. Even though some research milestones have been achieved yearly through bench-scale coagulation experiments, a large-scale practical application has not been proven. The lack of PBNC practicality and commercialisation is mainly due to several disadvantages associated with PBNCs, as mentioned in Sections 1 and 2 of this review.

Choy et al. [121] and Saleem and Bachmann [115] have noted that financial capabilities, framework directives, market awareness, and research development are among the challenges faced by PBNC progression. Until the known disadvantages of PBNCs are overcome, extensive application and commercialisation of PBNC will remain a future possibility.

Finding alternatives to chemical coagulants is necessary, and PBNCs are promising. They are suitable and environmentally friendly alternatives. The following are necessary for PBNCs to be successfully and realistically applied commercially: (1) Raw material sources

must be abundant and easily accessible. (2) Competition in meeting food demand needs to be eliminated by focusing research on non-edible plants that are generally nontoxic, easily cultivated, and available free of charge. It should be noted, however, that some non-edible plants are used for medicine. Therefore, the high use of such plants in water treatment could affect their supply to the medical sector. Hence, their availability needs to be enhanced [119]. (3) Modification in PBNCs should be encouraged, and modification parameters should be optimised to achieve highly efficient products that meet commercialisation requirements as natural coagulants.

3. Conclusions

The likelihood of plant-based natural coagulants being an alternative to chemical coagulants in water and wastewater treatment is high. This is especially the case with the employment of a modification method that alters the native properties of materials to the desired properties necessary for plant-based natural coagulants' application in coagulation and flocculation processes. Grafting copolymerisation methods are the most used methods. Microwave-assisted grafting copolymerisation has been shown to be the most recommended due to its environmentally friendly nature; high grafting efficiency, with a high yield of the copolymer; and relatively short time requirement.

Process optimisation using response surface methodology, with the choice of the best design, will lead to achieving optimum conditions of the significant factors necessary to achieve high grafting efficiency, and high treatment performance in the coagulation and flocculation processes. Two designs have been shown to be the most commonly used, the Box–Behnken design and the central composite design. Their advantages and disadvantages have been outlined. Box–Behnken design has been shown to be less expensive as it requires a smaller number of experimental runs and design points fall within safe operating zones.

Furthermore, characterisation techniques may be employed to evaluate the physiochemical properties of native material, to determine what is required to achieve high-performance efficiency. Further characterisation of modified material via microwave-assisted copolymerisation will be conducted to confirm the modification process and determine the presence of the features necessary for flocculating activity. Treatment mechanisms could also be predicted from the characterisation results.

In-depth research on the modification and optimisation of plant-based natural coagulants (PBNCs) may actualise the practicality of their usage as an alternative to chemical coagulants. Enhancing PBNCs' physiochemical properties may result in overcoming the disadvantages associated with their application. The future of PBNCs is promising, as the modified material is stable and suitable for application, which will enable their technological advancement to allow potential commercialisation. Future research may focus on the comparative analysis of modified PBNCs that have been proven to have high treatment performance, against the most used chemical coagulants. The aim of the analysis may be to rank the best alternative in terms of treatment efficiency, cost of material, biodegradability, and biocompatibility. Moreover, high emphasis is placed on research targeting the commercialisation potential of plant-based natural coagulants.

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