A Review on Development and Application of Plant-Based Bioflocculants and Grafted Bioflocculants

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A Review on Development and Application of Plant-Based Bioflocculants and Grafted Bioflocculants

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Supporting Information

ABSTRACT: Flocculation is extensively employed for clarification through sedimentation. Application of eco-friendly plant-based bioflocculants in wastewater treatment has attracted significant attention lately with high removal capability in terms of solids, turbidity, color, and dye. However, moderate flocculating property and short shelf life restrict their development. To enhance the flocculating ability, natural polysaccharides derived from plants are chemically modified by inclusion of synthetic, nonbiodegradable monomers (e.g., acrylamide) onto their backbone to produce grafted bioflocculants. This review is aimed to provide an overview of the development and flocculating efficiencies of plant-based bioflocculants and grafted bioflocculants for the first time. Furthermore, the processing methods, flocculation mechanism, and the current challenges are discussed. All the reported studies about plant-derived bioflocculants are conducted under lab-scale conditions in wastewater treatment. Hence, the possibility to apply natural bioflocculants in food and beverage, mineral, paper and pulp, and oleo-chemical and biodiesel industries is discussed and evaluated.

1. INTRODUCTION

Flocculation is one of the important separation processes that are extensively employed in potable water or domestic or industrial wastewater treatment. Various types of flocculants have been developed and marketed for the removal of environmental-concern parameters such as suspended and dissolved solids, turbidity, chemical oxygen demand (COD), color, and dye through sedimentation. They have been applied in a diverse range of wastewaters such as food and beverages, paper manufacturing, agricultural production, dyes or textile, municipal, and others.[5] One of the leading manufacturers of flocculants (BASF: Badische Anilin- and Soda-Fabrik) reported that the global market for cationic polyacrylamide flocculants is worth around € 1.0 billion and is growing at 4% to 5% per year.[6] Through the addition of flocculant(s), finely suspended or dispersed particles are aggregated together to form flocs into the size for speedy sedimentation and clarification. The conventional flocculants used in treatment of water and industrial effluents can be classified into two categories depending on the chemical compositions: inorganic flocculants and organic polymeric flocculants.

Inorganic flocculants (salts of multivalent metals like aluminum and iron) are commonly being used because of low cost, ease of use, and availability. Nevertheless, their usage has been reduced and controlled because of some disadvantages such as a large amount is required for efficient flocculation, high sensitivity to pH, applicable to only a few dispersed systems, and inefficient toward very fine particles.[7] Acidic or alkaline solutions are always needed to alter the pH of the wastewater in order to achieve its isoelectric point and form a complex metal hydroxide for precipitation or sedimentation.[8] Generally, inorganic flocculants are cationic-based and the impurity particles are negatively charged. The flocculation mechanism involved is either charge neutralization or patching where the flocs formed with the mechanism as shown in Figures 1 and 2 are loosely packed and settled slowly.[9] Besides, its application has caused problems of increased metal concentration or residual aluminum in treated water which may have human health implications, and produces a large quantity of sludge, the disposal of which itself is another problem.[7,10]

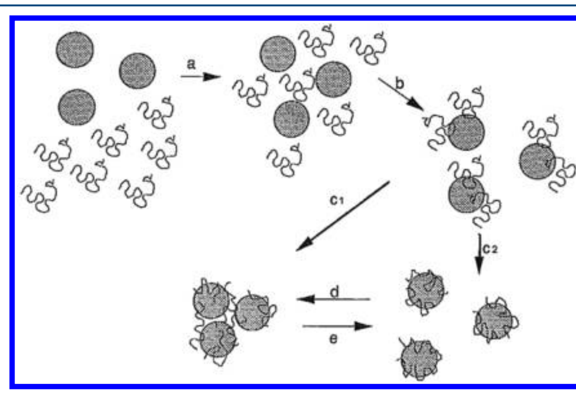

Figure 1. Action of charge neutralization of cationic flocculant with the particle surface[11]

Organic polymeric flocculants such as polyacrylamide have become very important in wastewater treatment because of their remarkable ability to flocculate even when added in small quantities (ppm).[7] High molecular weight polymers with long

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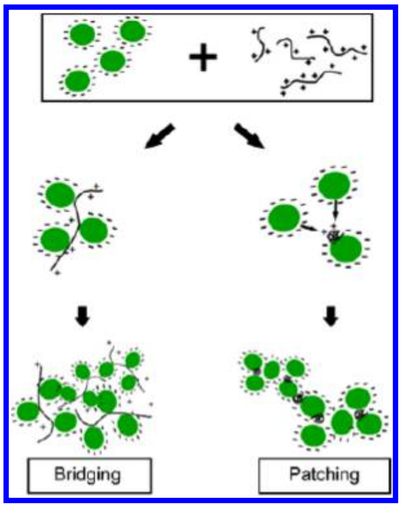

Figure 2. Flocculation mechanisms of bridging and patching[12]

chain are absorbed on particles as shown in Figure 2 with loops and tails extending into solution, and give the possibility of attachment of these "dangling" polymer segments onto other particles, thus "bridging" particles together.[13] Hence, the flocs formed are bigger, stronger, and denser with good settling characteristics.[14] In addition, they are easy to handle, immediately soluble in aqueous systems, not sensitive to pH, and produce lower sludge volume.[10] However, the potential problems associated with their use are lack of biodegradability and dispersion of monomers or residual polymers in water that may represent a health hazard.[10,13,15] Sludge formed at water treatment plants with polymeric flocculants has a limited potential for recycling due to the nonbiodegradability of synthetic polymers.[1]

With increasing awareness of potential harms caused by chemical flocculants and implementation of more stringent environmental regulations, some countries (e.g., Japan, Switzerland, and France) have started to strictly control its usage in drinking water treatment and food-related processing.[13,16] Researchers are trying to discover highly efficient and eco-friendly bioflocculants with the aim to replace the conventional flocculants. Biopolymers-based flocculants have attracted wide interest from researchers because they have the advantages of biodegradability and being nontoxic and easily available from reproducible agricultural resources.[10,14,17]

Natural organic flocculants which are based on natural polymers or polysaccharides like starch, cellulose, chitosan, natural gums, and mucilage, etc. have been investigated for their flocculating properties in wastewater treatment. Chitosan (amino-polysaccharides) has received a great deal of attention in the last decades in water treatment processes for the removal of particulate inorganic or organic suspensions and dissolved organic substances.[10] Starch itself may be used as flocculant; however, its flocculation efficiency is low. As a result, starch is generally modified in order to obtain products with good flocculation efficiency and has been applied in treating wastewater[18,19] and in the papermaking industry.[20] Sodium carboxymethylcellulose (CMCNa) is produced by chemical modification of cellulose and has been tested as eco-friendly flocculants for drinking water treatment.[21] Natural gums, such as guar gum and xanthan gum have been studied extensively as effective flocculants over a wide range of pH and ionic strengths for treatment of wastewater from various industries.[22,23]

The plant-based bioflocculants contain natural polysaccharides which are suspected to exhibit excellent selectivity toward aromatic compounds and metals, thus efficient in the removal of pollutants from wastewater.[24] However, it was reported that their feasibility is restricted by moderate flocculating property and short shelf life.[25] In recent years, grafted bioflocculants are developed and claimed to have remarkable flocculating ability and biodegradability. As shown in Figure 3, natural biopolymers

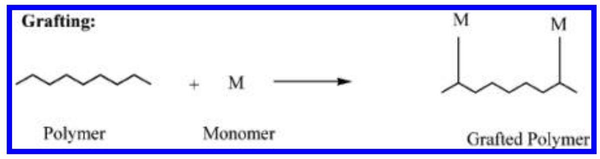

Figure 3. Schematic representation of the grafting method in polymer modification[27]

are covalently bonded (modified) by inclusion of synthetic monomers (e.g., acrylamide) onto their backbone to synthesize the high molecular weight grafted copolymers that exhibit improved flocculating properties.[26]

The rising concern of environmental pollution problems and health-concerning issues causes the utilization of bioflocculants derived from natural sources to be important progress in sustainable environmental technology. In this review, the development and flocculating abilities of plant-based bioflocculants and grafted bioflocculants are reported for the first time. The preparation methods of plant-based bioflocculants and the grafting methods of grafted copolymers are presented and reviewed. Their flocculating effectiveness in wastewater treatment and the relevant flocculating mechanisms are investigated in detail. This review is aimed to provide a clear and comprehensive conspectus about the research progress in developing plant-based bioflocculants and grafted bioflocculants, the current challenges and future perspectives, and the potential application of plant-based bioflocculants in diverse industries.

2. PLANT-BASED BIOFLOCCULANTS

Natural plant-based bioflocculants emerge as an attractive alternative to polymeric flocculants, and their application in wastewater treatment has become increasingly essential in light of their biodegradability, nontoxicity, wide availability from renewable resources, environmental friendly processing, and having no negative impact on the environment. The applications of plant-derived biopolymers for treatment of various types of wastewater have been discovered and reported. Plant-based bioflocculants derived from some plant species (*Hibiscus/Abelmoschus esculentus*, *Malva sylvestris*, *Plantago psyllium*, *Plantago ovata*, *Tamarindus indica*, and *Trigonella foenum-graecum*) have shown promising results with respect to the treatment of biological effluent, landfill leachate, dye-containing wastewater, textile wastewater, tannery effluent, and sewage effluent.[1,3,4,28]

2.1. Plant Materials and Bioflocculants Preparation Methods. Table 1 shows six different types of plants which have been investigated for their flocculating properties in the treatment of synthetic or genuine wastewater. It is discovered that all plants being studied for flocculants production have one similarity. All of them have a mucilaginous texture with polysaccharides as the main component and they have a neutral pH by nature. Mucilage is plant hydrocolloids that have viscous

Table 1. Plants That Have Been Investigated of Their Flocculating Properties

plant species								
scientific name	common name	charge	pH	solubility in water	active ingredients	extraction method	extracted plant part	ref
Hibiscus/ Abelmoschus esculentus	okra/lady finger	anionic	5.2 to 8	soluble in cold water	L-rhamnose, D-galactose and L-galacturonic acid	solvent extraction and precipitation, drying and grinding	seedpods	1, 32–37
Malva sylvestris	mallow		6.5 to 7			drying and grinding	seedpods and lobs	1
Plantago psyllium	psyllium	anionic	7.11 to 7.84	soluble in cold water	L-arabinose, D-xylose and D-galacturonic acid	solvent extraction and precipitation	seed husk	2,3, 38
Plantago ovata	isabgol	anionic				drying and grinding	seed husk	28
Tamarindus indica	tamarind			soluble in cold water	D-galactose, D-glucose and D-xylose	solvent extraction and precipitation	seeds	4
Trigonella foenum-graecum	fenugreek	neutral	7.73 to 8.62	partially soluble	D-galactose and D-mannose	solvent extraction and precipitation	seeds	37,39, 40

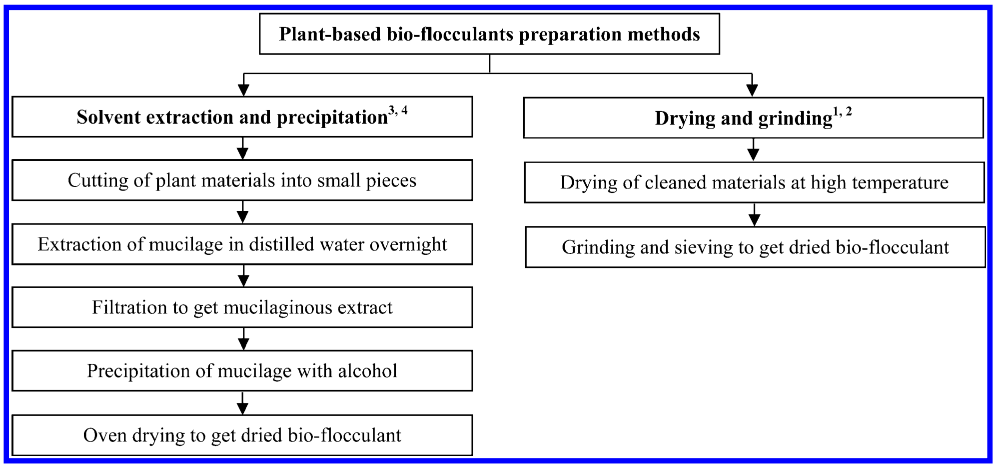

Figure 4. Preparation methods of plant-based bioflocculants.

colloidal dispersion properties in water. They are heterogeneous in composition and are typically polysaccharide complexes formed from the sugars of different monosaccharides, including arabinose, galactose, glucose, mannose, xylose, rhamnose, and uronic acid units.[29−31] It is predicted that some of the active ingredients in the mucilage are responsible for the flocculating property. Therefore, extraction becomes the essential step to isolate the active components that exhibit the flocculating activity from the plants. However, the investigation of active constituents that are corresponding with the flocculating ability is limited.

There are two methods for the production of plant-derived bioflocculants which have been reported thus far: (i) solvent extraction and precipitation[2,3,33,36−41] and (ii) drying and grinding.[1,28] The detailed procedures for each method are illustrated in Figure 4. The methodologies used to produce the bioflocculants are environmental-friendly, do not use toxic chemical, and are easy and simple. As listed in Table 1, the solvent extraction and precipitation method has been applied for extraction of bioflocculants from okra, psyllium, tamarind, and fenugreek. The cleaned plant materials were extracted with distilled water for overnight, and the filtered mucilaginous extract was then precipitated by using alcohol. The drying and grinding method was used for preparation of bioflocculants from mallow, okra, and isabgol. The cleaned materials were dried at high temperature, and then ground and sieved to obtain the bioflocculants. It was discovered that the bioflocculants obtained had lower flocculating activity. Low removal efficiency of COD, color, and suspended solids (SS) at 17, 27, and 41%, respectively, was reported when they were used as flocculant in treatment of landfill leachate with a direct flocculation process.[28] They were found to be more effective in a coagulation−flocculation process in which a coagulant was added before bioflocculant. On the other hand, the bioflocculants that are prepared with solvent extraction and precipitation displayed excellent flocculating ability in the treatment of wastewater with a direct flocculation process for which no coagulant and pH adjustment were required. This finding indicated that the extraction step is closely related to flocculating efficiency and plays the major role in the extraction of the active constituents with high flocculating activity from the plant materials.

To date, all the studies that investigated the flocculating property of bioflocculants only paid attention to the flocculation process and analyzed the effects of flocculant dose, contact time, and pH on the flocculation efficiency.[2,3,40] There is no published study that investigates the relationship between extraction and flocculation. It is very important to relate the extraction methods and conditions with the flocculating activity, evaluate the extraction parameters that may degrade the flocculating efficiency of the products, and optimize the extraction conditions in order to produce the most efficient bioflocculants that are comparable to commercial flocculants in terms of cost and flocculating efficiency.

2.2. Flocculation Efficiency. The jar test[42] is used to evaluate the flocculating abilities of the plant-based bioflocculants and optimize the flocculation process in most studies. The identified usage of natural flocculants and their technical

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Table 2. Flocculating Efficiencies of Plant-Based Bioflocculants

plant-based bioflocculant (preparation method)	treated wastewater	sedimentation period (min)	optimum pH	optimum coagulant dose (mg/L)	optimum bioflocculant dose (mg/L)	flocculation efficiency: types of removal	flocculation efficiency: % removal	ref
isabgol (drying and grinding)	semiaerobic landfill leachate	120	6.5 to 7.5	7200	400	COD	64	28
						color	90	
						SS	96	
psyllium (extraction and precipitation)	golden yellow dye and reactive black dye	10	4 and 7		10	dye	71.4 and 35	3
	textile	60	4		1.6	SS	92.4	2
			7			TDS	68.76	
	sewage and tannery	60	7		1.2	SS	94.69 and 87.03	38
tamarind (extraction and precipitation)	golden yellow dye and direct fast scarlet dye	60	7		10 and 15	dye	60 and 25	4
	azo dyes, basic dyes and reactive dyes	10	6, 9.2, and 1		10, 10, and 15	dye	36.43, 38.96, and 52.13	41
fenugreek (extraction and precipitation)	tannery	60	7		0.08	SS	85	40
						TDS	40	
	sewage	60	9.2		0.16	SS	97.15	39
						TDS	19.9	
okra (extraction and precipitation)	tannery	60	9.2		0.04	SS	95	36
						TDS	69	
	sewage	60	4		0.12	SS	86.86	33
			7			TDS	>95	
okra and fenugreek (extraction and precipitation)	textile	60	9.2		0.8 and 0.04	SS	98 and 94.2	37
						TDS	31.6 and 43.7	
						color	53.47 and 6	
mallow and okra (drying and grinding)	synthetic (kaolin)	10, 20, 30	6.2 and 6	8.6	12 and 5	turbidity	97.4 and 97.3	1
	biologically treated effluent			171.1	62.5 and 2.5		67 and 74	

viability for industrial wastewater are currently limited to only academic research. Their flocculating performance reported in literature has been compiled and summarized in Table 2. The findings indicated their good flocculating potential for various types of industrial wastewater treatment. Some of them are effective in low concentrations and comparable to synthetic flocculants in terms of treatment efficiency.[33,40] Fenugreek[40] and okra[33] mucilage were proven to be as effective as commercial flocculant (polyacrylamide) in the treatment of tannery effluent and sewage wastewater.

As reported in the previous section, bioflocculants obtained with drying and grinding exhibit lower flocculating efficiency. These bioflocculants must be coupled with the use of coagulant in a coagulation−flocculation process. Table 2 shows that the Isabgol husk prepared with drying and grinding was effective as a coagulant aid for the treatment of landfill leachate with poly(aluminum chloride) (PACl) as the coagulant.[28] However, unsatisfactory results were obtained when it was used as primary coagulant aid without coagulant due to low surface charge. Another recent study showed that the dried and ground mallow and okra bioflocculants were efficient in removing turbidity from a synthetic kaolin suspension and biologically treated effluent when aluminum sulfate was used as the coagulant.[1] Alternately, the bioflocculants extracted with water as the solvent display remarkable flocculating performance in a direct flocculation process. High removal efficiency of solids either in suspended (SS) or dissolved forms (TDS), dye, turbidity, and color was achieved by using a low concentration of bioflocculant dosage. For instance, 95% removal of SS in treatment of tannery wastewater[36] and >95% removal of TDS in treatment of sewage effluent[33] were attained with 0.04 mg/L and 0.12 mg/L of okra bioflocculant. Mallow and okra bioflocculants were reported to have high efficiency in turbidity removal at 97% in the treatment of synthetic (kaolin) wastewater.[1] In another paper, dye removal as high as 71%[3] and color removal at 53%[37] were achieved by using psyllium and okra bioflocculants, respectively.

As shown in Table 2, a long sedimentation period (60 and 120 min) was reported in some literature. It is postulated that the flocs formed are weaker and smaller in size and thus a longer settling time is required. In the study of *Tamarindus indica* (Tamarind) as bioflocculant, it was not suggested as an effective flocculant for the removal of vat (golden yellow) and direct (direct fast scarlet) dyes from textile wastewater because of unsatisfied dye removal after a long period of contact time.[4] In most of the reported studies, the suitable pH range was neutral for maximum flocculating efficiency of bioflocculants. Some were reported to be workable in acidic or alkali condition depending on the type and characteristics of treated wastewater.

2.3. Flocculation Mechanism. The most common mechanisms of flocculation include charge neutralization, electrostatic patch, and polymer bridging.[13] The flocculation mechanism of charge neutralization is only applicable when the colloid suspended particles and the added flocculants are of opposite charge.[13] In many cases, impurity particles are negatively charged. As shown in Table 1, the ionic charges of bioflocculants are anionic for okra, psyllium and isabgol, neutral for fenugreek, and unknown for mallow and tamarind. Since most of the bioflocculants are verified to be either anionic or neutral, it is presumed that charge neutralization is not the responsible mechanism. Thus, the most probable mechanism that happened between plant-derived bioflocculants with particulate matter in effluent is polymer bridging in which the biopolymers serve as a bridge based on particle−polymer−particle complex formation. The bridging mechanism involved in bioflocculation as shown in Figure 5 has been reported in a study that used one flocculating microalgae to concentrate the nonflocculating microalgae of interest.[12]

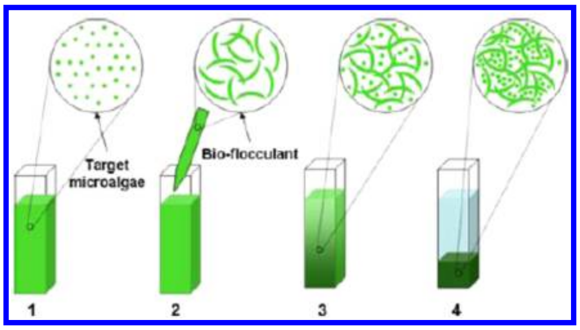

Figure 5. Bridging mechanism in bioflocculation of microalgae.[12]

To be effective in destabilization, a biopolymer molecule must contain chemical groups (free hydroxyl group), which comprise the possible binding sites that can interact with sites on the surface of the colloidal particles. When a biopolymer molecule comes into contact with a colloidal particle, some of these groups adsorb at the particle surface, leaving the remainder of the molecule extending out into the solution. If a second particle with some vacant adsorption sites contacts with these extended segments, attachment will occur. A particle−polymer−particle complex is thus formed in which the biopolymer serves as a bridge.[41] Polymer bridging has been proposed as the plausible mechanism for flocculation behavior in treatment of textile wastewater with *Plantago psyllium* mucilage[3] and *Tamarindus indica* mucilage.[4] For other bioflocculants, the underlying mechanism has not been predicted or reported up to date.

In some studies, X-ray diffractograms were used to observe and postulate the possible mechanism underlying the flocculating property of natural polymers.[2,33,38−40] However, X-ray diffraction patterns did not give any specific evidence for the mechanism of flocculation, but it suggested the interaction of the solid waste with the mucilage. In those studies,[2,33,38−40] the formation of different crystal types were observed after the solid waste was treated with polysaccharide, and this indicated the change in the nature of the crystalline waste material in the wastewater during the flocculation process. This may be due to the interactions between free hydroxyls groups of the polysaccharide and the contents of the wastewater.

As the chemistry of coagulation and flocculation primarily depends on the electrical properties, an analysis of zeta potential was used as a measurement of the magnitude of electrical charge surrounding the colloidal particles and explained the removal mechanisms of the flocculation process.[28] Through measurement of zeta potential, the ionic charge of the bioflocculants and the surface charge of the suspended particles can be defined, and this information is useful to predict the plausible flocculation mechanism. Recent studies showed that light diffraction scattering (LDS) is a useful technique to monitor the dynamics of flocculation and use as a tool to evaluate different types of flocculation mechanism depending on the flocculants characteristics.[43,44] LDS enabled an evaluation of the effects of charge density of the flocculant on the fractal dimension of the flocs, which serves as the measurement on the compactness of the aggregates. As a summary, performance of the bioflocculants during flocculation could be monitored by a combination of the measurement of zeta potential and the LDS technique. The flocculation kinetics and mechanism of the bioflocculants could then be determined.

2.4. Current Challenges and Future Perspectives. Even though most of the studies have proven that the bioflocculants were workable and effective for treatment of various types of wastewaters, all these researches were carried out at laboratory scale and only tested in the treatment of wastewaters. There are many factors that restrict its development and application in industry. The four major problems include sensitivity of bioproducts to preparation process, fast degradation with time, moderate flocculating efficiency, and higher cost compared to commercial flocculants.

The functional properties of the hydrocolloid mucilage are sensitive to the preparation methods and could be altered by the drying processes to a great extent.[45] In addition, the chemical composition and molecular structure of hydrocolloids often depend on the source, extraction methods, and any further processing conditions.[30] For instance, the rheological properties and viscoelastic behavior of natural plant gums depend on the method and condition of extraction, purification, drying, and further modification processes.[46] Thus, more investigation concerning the processing methods and conditions (preparation, extraction, purification, drying, and storage) of bioflocculants is strongly important because it will determine the quality and stability of bioflocculants.

Biopolymers face degradation of products with time and processing parameters or conditions.[29] Fresh mucilage is susceptible to microbial attack due to its high water activity and composition, and reducing its shelf life to a few days at room temperature.[47] In addition, the flocs tend to lose stability and strength with time because of their biodegradability.[48] Materials with reduced moisture content will resist germination under favorable conditions, thus prolonging the storage life. Therefore, the drying process is of vital importance to produce high quality bioflocculants in which the desired active constituents with flocculating property could be well preserved and the storage period could be extended.

Some natural flocculants are moderately effective and are needed in huge dosage compared to synthetic flocculants because of their relatively lower molecular weight and shorter shelf life.[25] Hence, an optimization study of processing, extraction, and drying conditions is highly important to get the optimum conditions that can produce the bioflocculants with maximum yield and flocculating ability.

Another significant drawback of using bioflocculants is the processing and production cost which is higher than conventional flocculants. Yet, this drawback can be overcome because of the major importance of their applications in food and other industries, allowing for a price premium product, and its substantial benefit to environment and human health. The phytonutrients associated in the bioflocculants will further enhance the quality of the products too.

Nonetheless, the future development of cost-effective and environmental-friendly plant based bioflocculants that exhibit high flocculating ability as an attractive alternative to replace commercial flocculants in food, cosmetic, pharmaceutical, and other industries is highly possible. Intensive research efforts

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related to bioflocculants should continue and be in-line with environment and health protection.

2.5. Possible Application of Plant-Based Bioflocculants in Different Industries. To date, there is no detailed study about the applicability or feasibility of plant-derived bioflocculants in other industries apart from wastewater treatment. Their application studies are only at a preliminary level and conducted on a laboratory basis. Exploration of application boundaries to new areas of industrial interest instead of focusing on downstream processes (wastewater treatment) is highly important to increase the market need of this product. In fact, there are many processing industries utilizing a clarification or flocculation process in the manufacturing of certain products. The clarification or flocculation methods or agents used in different industries are summarized in Table 3.

Consumers are becoming more health conscious, increasingly aware of what they consume and concern of the nutritional value of food materials and ingredients. Safe and healthy products and environmental-friendly processing are preferred and will be the primary concern in many industries. Many of the conventional clarification and flocculation methods listed in Table 3 have their own drawbacks. It has become necessary to study a new clarification or flocculation method/agent with the objective of securing a safe and high quality product. In this respect, plant-based bioflocculants may emerge as an attractive option to alleviate the problems mentioned above; and at the same time enhance the nutritional value of the products. The background and detailed explanation for natural bioflocculants that could be a suitable alternative to the current flocculation/clarification methods in the food and beverage, mineral, paper-making, oleo-chemical, and biodiesel industries are attached in Supporting Information.

Plant-based bioflocculants have been proven to remove impurities, turbidity, organic and inorganic loads, and suspended and dissolved solids effectively. Besides, natural water-soluble polysaccharides have the capability of flocculating small particles.[38] The long chain of polysaccharides has the ability to bind or bridge different components and result in efficient removal of undesirable compounds. Okra,[36] fenugreek,[40] and psyllium[38] bioflocculants could remove the proteinaceous matter effectively which surrounds the colloidal particles and the metallic ions in tannery effluent. In addition, they have been verified to have the ability to remove or reduce the inorganic and organic solids, metals, fibers, and toxic pollutants from textile and sewage wastewaters.[2,39] Thus, they may exhibit the capability to clarify the juices extract, flocculate, and recover the muscle proteins from seafood and meat processing byproducts and improve the retention of fibers and fillers in the papermaking industry.

A study showed that okra and mallow bioflocculants exhibited the flocculating ability to effectively remove the turbidity from a kaolin suspension solution.[1] Therefore, a plant-based bioflocculant may be applied to produce a high brightness and whiteness coating clay, which contains a minimum amount of undesirable residual chemicals particularly for application in the cosmetic and pharmaceutical industries.

In the oleo-chemical industry, the use of natural bioflocculants is postulated to have the advantages of a simple process with reduced number of operations, lower purification time, lower treatment cost, and mild conditions of treatment with low temperature and pressure. By using natural bioflocculants, strong and dense flocs could be formed in a

Table 3. Clarification/Flocculation Process in Different Industries

	application area	separated components	clarification/flocculation method/agent	ref
beverage industry	clarification of wine	iron compounds, suspended solids, proteins, dead yeast cells	activated carbon, gelatin, albumen, bentonite	49−52
	clarification of vinegar	iron compounds, suspended solids, proteins	activated carbon, gelatin, albumen	49, 50
	clarification of fruit juices	suspended particles, proteins, polyphenols, pectins, carbohydrates	gelatin, bentonite, kieselsol, silica sol, polyvinylpolypyrrolidone (PVPP) or combination of these compounds, chitosan	53−57
	clarification of dates extract	nonsoluble matter, coloring matter and semisoluble (e.g., pectin) material	activated carbon, bentonite, PVPP	58, 59
	clarification of sugar cane juice	organic and inorganic constituents, suspended solids	lime, bentonite, activated carbon, polyacrylamide polymer	60−63
food industry	recovery of muscle proteins from fish processing byproducts	bones, scales, skin, fats	isoelectric solubilization/precipitation, polymeric flocculants (anionic, nonionic and cationic)	64, 65
	recovery of muscle proteins from meat processing byproducts	bones, scales, skin, fats	isoelectric solubilization/precipitation, mechanical deboning	66−68
mineral industry	clarification of kaolin slurry	discolouring contaminants (e.g., titanium, iron), organic and inorganic carbon, impurity clay minerals	anionic polymeric flocculants (e.g., polyvinyl alcohol, polyacrylamide)	69−71
paper industry	retention of fine matters during papermaking	cellulose fines, fiber fines and fillers	polyelectrolytes flocculants (e.g., polyacrylamides, poly aluminum chloride, poly(ethylene oxide)), modified starches, chitosan	20, 43, 72−76
oleo-chemical or biodiesel industry	clarification of crude glycerol	methanol, inorganic salt (catalyst residue), free fatty acids, lipids, unreacted mono- or di- or triglycerides, nonglycerol organic matters	chemical treatments, physical treatments (gravitational settling, centrifugation, evaporation, distillation), micro and ultrafiltration	77−82

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Table 4. Flocculating Efficiencies of Plant-Based Grafted Bio-flocculants

plant-based grafted bioflocculant	grafting method	treated wastewater	sedimentation time	optimum dose (ppm)	flocculation efficiency: type of removal	flocculation efficiency: results	ref
polyacrylamide-grafted-*Plantago psyllium* (Psy-*g*-PAM)	conventional free radical	tannery and domestic wastewater	1 hour	60	SS	>95% and >89%	93
		textile wastewater	1 hour	1.6	SS	>93%	94
					TDS	72%	
					color	15.24%	
polyacrylonitrile-grafted-*Plantago psyllium* (Psy-*g*-PAN)	conventional free radical	textile effluent	1 hour	1.6	SS	94%	95
					TDS	80%	
		tannery effluent	1 hour	1.2	SS	89%	87
					TDS	27%	
polymethacrylic acid-grafted-*Plantago psyllium* (Psy-*g*-PMA)	microwave-assisted	municipal sewage wastewater	25 min	2.5	turbidity	100 to 12NTU	96
					SS	117 to 14 ppm	
					TDS	291 to 212 ppm	
polyacrylamide-grafted-*Plantago ovata*	microwave-initiated	0.25% kaolin suspension	15 min	0.75	turbidity	59 to 22NTU	92
		1% coal fine suspension			OD	1.5 to 0.25	
poly(methyl methacrylate)-grafted-*Plantago ovata*	microwave-assisted	0.25% kaolin suspension	15 min	1	turbidity	185 to 70NTU	97
polyacrylamide-grafted-*Tamarindus indica* (Tam-*g*-PAM)	conventional free radical	textile wastewater	10 min	5	Azo dye	43%	41
					basic dye	27−29.6%	
					reactive dye	26.8−32.3%	
polyacrylamide-grafted-tamarind kernel polysaccharide (TKP-*g*-PAM)	microwave-assisted	kaolin suspension	15 min	0.5	turbidity	125 to 6NTU	98, 99
		municipal sewage and textile industry wastewaters		9	turbidity	58 to 14NTU and 97 to 80NTU	
					SS	335 to 55 ppm and 295 to 50 ppm	
					TDS	265 to 205 ppm and 345 to 295 ppm	
					COD	540 to 205 ppm and 586 to 295 ppm	
hydrolysed polyacrylamide-grafted-tamarind kernel polysaccharide (Hyd. TKP-*g*-PAM)	microwave-assisted	kaolin suspension	15 min	0.5	turbidity	125 to 6NTU	91
		municipal sewage wastewater		9	turbidity	58 to 6NTU	
					SS	335 to 20 ppm	
					TDS	265 to 190 ppm	
					COD	540 to 155 ppm	

short time. After sedimentation, the formed flocs are easily separated through sedimentation. Since no chemical is used in the purification process, purified glycerol could be applied safely for a range of application in pharmaceutical or cosmetic industries. It is predicted that the bioflocculants may consist of adsorption sites (e.g., free hydroxyl groups and hydrogen bonding sites) that have strong affinity to remove the undesirable matters or components from crude glycerol.

3. PLANT-BASED GRAFTED BIOFLOCCULANTS

In recent years, considerable interest has been shown toward the chemical modification of natural macromolecules, especially polysaccharides, to improve their flocculating properties.[83,84] Such modification is done to overcome the drawbacks in term of moderate flocculation performance, uncontrolled biodegradability, and varying efficiency due to different processing conditions.[85] The biodegradability of natural polysaccharides needs to be suitably controlled[86] to prolong the shelf life and improve the flocculating ability. On the other hand, synthetic flocculants are highly effective and have long shelf life, but they are nonbiodegradable and toxic to environment.[17,87] The improvement in the properties of natural and synthetic polymers can be performed by developing grafted copolymers.[88]

Graft copolymerization is aimed to obtain a novel tailor-made polymer with the best properties of both groups. It has been proven that efficient, reasonably shear stable and eco-friendly flocculants can be developed by grafting synthetic polymer branches onto the rigid backbone of natural ones.[88] Some studies showed that acrylamide-grafted natural polymers, such as amylopectin, guar gum and xanthan gum, starch, and sodium alginate find extensive application as flocculants.[89,90] Recently, common polymers such as polyacrylamide have been grafted onto the backbone of plant-based biopolymers (*Plantago ovata*, *Plantago psyllium*, and *Tamarindus indica*) and showed significant improved flocculating properties compared to ungrafted natural polysaccharides.[91−93] The flocculating performance of all the plant-based grafted bioflocculants reported in literature is summarized in Table 4.

3.1. Grafting Methods. Grafted copolymers consist of a long sequence of one polymer with one or more branches of another polymer.[100] With the help of preformed polymer (polysaccharide in the case of grafted polysaccharides) the synthesis of graft copolymer process will start. The free radical sites will be created on this preformed polymer with the help of

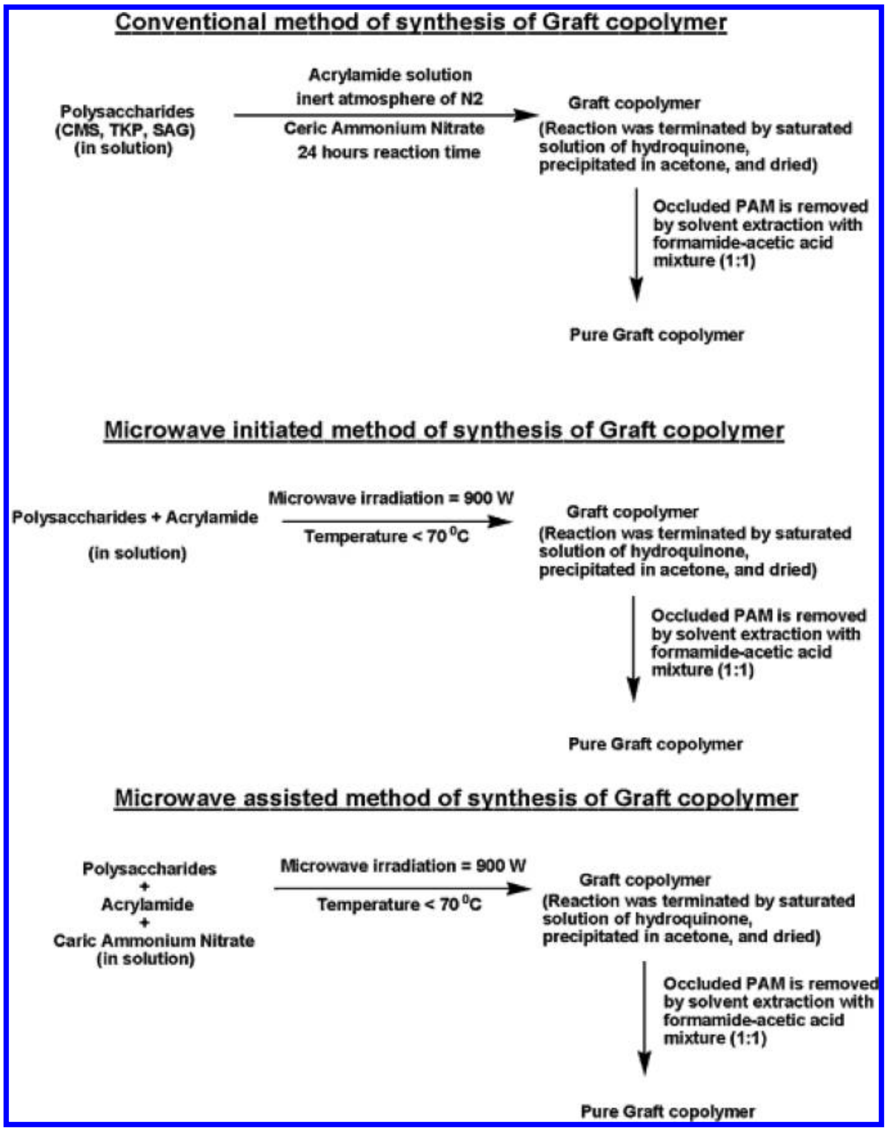

Figure 6. Schematic representation for the synthesis of grafted copolymers using conventional, microwave-initiated, and microwave-assisted method[99]

an external agent. The agent should be effective enough to create the required free radical sites, and at the same time should not be too drastic to rupture the structural integrity of the preformed polymer chain. Once the free radical sites are formed on the polymer backbone, the monomer can be added up through the chain propagation step, leading to the formation of grafted chains.[84,101] Conventional redox, microwave-initiated, and microwave-assisted grafting methods have been reported to have successfully synthesized plant-based grafted bioflocculants.[92,97−99] Figure 6 shows the synthesis of grafted copolymers of carboxymethyl starch (CMS), tamarind kernel polysaccharide (TKP), and sodium alginate (SAG) with acrylamide as monomer by using a conventional, microwave-initiated, and microwave-assisted method.[99]

Conventional redox (or conventional free radical) grafting method using chemical free radical initiators (e.g., ceric ammonium nitrate (CAN))[41,87,93−95] with nitrogen as the inert gas is commonly used to synthesize grafted copolymers. However, the conventional grafting method has the drawback of undesired homopolymer formation in the concurrent competing reaction. This would decrease the copolymer yield, contaminate the copolymeric product, and cause problems in the commercialization of the grafting procedures.[83] Normally, the process requires prolonged Soxhlet extraction using a mixture of formamide and acetic acid to remove all the homopolymer and/or unreacted substrates from the copolymer surface.[99,102] Moreover, the requirement of an inert atmosphere is an added disadvantage.

Recently, the synthesis of grafted copolymers used microwave-based techniques to alleviate the limitations in the synthesis of a range of grafted modified polysaccharide materials.[25,83] Synthesis can occur with a chemical free radical initiator (microwave-assisted technique)[89,103] or even without any chemical free radical initiator (microwave-initiated technique).[104] The microwave-based technique has certain advantages over other conventionally used techniques for free radical generation. The technique is reliable, easy to perform, and highly reproducible. Hence, microwaves offer a promising breakthrough for synthesis of grafted copolymers and encourage their further utilization in various applications.[83,84] As listed in Table 4, plant-based-grafted bioflocculants have been successfully synthesized with microwave-assisted and microwave-initiated techniques by using acrylamide or methacrylic acid as the monomers.[91,92,96,98,99] Grafted bioflocculants synthesized by microwave-initiated and microwave-assisted methods were proved to provide a better quality grafted copolymer with a higher percentage of grafting in comparison with a conventional redox grafting method.[98,99] Some research findings showed that the grafted copolymers synthesized by the microwave-assisted method presented superior flocculation characteristics when compared with grafted flocculants synthesized by conventional and microwave-initiated methods as well as with commercially available nonionic flocculant (Rishfloc 226 LV).[98,99]

Even though grafted bioflocculants synthesized with microwave technology present superior flocculating characteristics, its usage is concerned with high production cost. In the earlier studies, most of the grafting processes are carried out using domestic microwave ovens in which the irradiation power is generally controlled by on/off cycles of the magnetron.[83] Their use is not encouraged because of the safety concerns caused by insufficient control over the reaction temperature and pressure. To overcome these issues, modifications to domestic microwave ovens have been made, but their use is associated with high equipment cost which would increase the production cost of the copolymers and severely limit the application of grafted bioflocculants in developing countries. For microwave-based methods, proper care has to be taken to keep the reaction mixture below the boiling point. This is done to minimize the competing homopolymer formation and also to prevent formation of unwanted vapors, which may be toxic/carcinogenic because of the presence of acrylamide.[92]

3.2. Flocculation Efficiency. As shown in Table 4, plant-based grafted bioflocculants have been successfully synthesized and applied in the treatment of various types of wastewaters or effluents, and resulted in a higher decrease in environmental-concerned parameters such as solids, turbidity, dyes, and COD. Commonly, polyacrylamide is chosen for synthesis of grafted copolymers. Recent studies have shown that other types of chemical polymers such as polyacrylonitrile,[95] polymethacrylic acid,[96] and poly(methyl methacrylate)[97] were successfully used in the production of grafted bioflocculants with high removal capability in solids and turbidity.

As expected, the grafted bioflocculants have shown better flocculation efficacy than the natural polymers (ungrafted). This is due to the higher hydrodynamic volume (i.e., intrinsic viscosity) of the former[92] which leads to higher flocculation efficacy.[105] For example, *Plantago psyllium* mucilage grafted polyacrylamide (Psy-*g*-PAM) copolymer was proven to be a better flocculant than pure psyllium mucilage in the treatment of tannery and domestic wastewater.[93] In another study, polyacrylamide grafted *Tamarindus indica* mucilage (Tam-*g*-PAM) showed better flocculation efficiency than the pure mucilage for removal of various types of dyes from model textile wastewater containing azo, basic, and reactive dyes.[41] Another study reported that polyacrylamide grafted tamarind kernel polysaccharide (TKP-*g*-PAM) synthesized by microwave-assisted grafting method was superior to TKP and polyacrylamide-based commercial flocculant (Rishfloc 226 LV) in flocculation tests.[98]

In a study, hydrolyzed polyacrylamide-grafted tamarind kernel polysaccharide (Hyd. TKP-*g*-PAM)[91] was synthesized and shown to surpass the flocculation characteristics of unhydrolysed grafted copolymer (TKP-*g*-PAM) in treatment of kaolin suspension and municipal sewage wastewater. It was reported that after hydrolysis, the grafted chains become more straightened and expanded but still have flexibility compared with the unhydrolysed chains.[106] These properties result in a higher radius of gyration as well as pervaded volume and hence a higher flocculation efficiency obtained.[105]

The flocculating efficiency of grafted bioflocculants obtained with different grafting methods is compared in some studies. In a research work, the flocculation performance of the optimized grade of grafted copolymers (TKP-*g*-PAM) synthesized by the microwave-assisted method showed the best flocculation efficiency followed by the optimized grafted copolymers synthesized by the microwave-initiated method, and last the free-radical initiated grafting method in the treatment of synthetic wastewater (kaolin suspensions) and municipal sewage wastewater.[99] Another study[98] also shows that microwave synthesis process produced longer grafted copolymers (TKP-*g*-PAM) with higher molecular weight and displayed better flocculating efficiency compared to the grafted bioflocculant synthesized with the conventional method.

As a concluding remark, grafted copolymers synthesized by microwave-initiated and -assisted method display better flocculation efficiency with a higher percentage of grafting compared to the conventional redox grafting method.[99] The higher is the percentage of grafting, the longer the grafted chains with higher molecular weight and radius of gyration can be obtained. With an increase in molecular weight and radius of gyration, the approachability of the contaminants toward the grafted copolymers will be increased, and as a result better flocculation efficiency can be achieved.[105,107]

3.3. Flocculation Mechanism. For grafted bioflocculants, it was reported that an increase in chain length and molecular weight contributed to an increase in flocculation efficiency.[93] Polyacrylamide-grafted polysaccharides are mainly nonionic or anionic in nature[91] while the sustained organic and inorganic matters in wastewater carry low negative charges or positive charges. The possible reason for better flocculation characteristics of graft copolymers over the ungrafted bioflocculant is essentially because of the polymer bridging mechanism, because the segments of a polymer chain can adsorb onto different particles surface and form bridges between adjacent particles. The grafted bioflocculants exhibit the characteristics of long polymer chains (high molecular weight) and high radius of gyration; hence, the adsorbed polymer molecules tend to adopt a more extended configuration for interacting with more than one particle which leads to effective formation of a particle–polymer–particle complex (flocs).[86,108]

As reported in a study,[98] polymer bridging was responsible for the better flocculating property of the grafted copolymers over a linear polymer of which the segments of a polymer chain were adsorbed onto different particles, thus linking the particles together. Some studies[93,94] show that there was an optimal dosage at which the flocculation efficacy was maximum (i.e., the turbidity of the supernatant collected was minimum). Beyond the optimum dosage, the excess grafted bioflocculant would cause the aggregated particles (flocs) to redisperse in the suspension and would also reduce particle settling and finally decrease the flocculation (i.e., turbidity of the collected supernatant increases). This behavior of the flocculation curve was reported to correspond with the bridging mechanism involved behind the phenomenon.[87,92] Another study stated that because of the flexible polyacrylamide graft chains, the colloidal particles aggregate through the bridging effect and form larger net-like flocs. Then, with the help of enhanced approachability of the polyacrylamide chains, the larger flocs with net-like structure can further seize residual particles from water through a sweeping effect.[109] Finally, the compacted flocs are formed and settle down.

Most of the reported studies in this field are focused mainly in the application of grafted bioflocculants in wastewater treatment. The investigation of the flocculation mechanism is very limited. Since the chain length and molecular weight are the key factors to determine the main flocculation mechanism underlying the flocculating performance of grafted bioflocculants, it is proposed that measurement of molecular weight and observation of flocs formation with dynamic light scattering techniques for ungrafted and grafted bioflocculants could be applied to identify the responsible flocculation mechanism.

3.4. Current Challenges and Future Direction. The ongoing research on plant-based-grafted bioflocculants is conducted on laboratory scale in treatment of wastewaters or effluents. There are many factors that constrain its development and application to pilot scale or in other industries.

The monomer consumption and the chemicals used in the synthesis process may have the impact on the environment, and the application of these grafted bioflocculants in the food or pharmaceutical industries may cause health and safety issues. A study indicated that acrylamide is neurotoxic in animals and humans, and it has been shown to be a reproductive toxicant in animal models and a rodent carcinogen.[110] For acrylonitrile, studies showed that it is a mutagen, a tetratogen, and a carcinogen.[102] This factor would limit its application in those industries that produce human consumed products.

Another problem is the complexity of the synthesis process. To synthesize grafted copolymers, the plant-derived bioflocculant is produced first, followed by grafting of monomers onto the backbone of polysaccharides. The whole production process is much more time and energy consuming compared to the production of plant-based bioflocculants. In addition, even though it was stated in the literature that the grafted bioflocculants are biodegradable to a desirable extent, no study has been conducted to prove it, and their biodegradability is still unknown.

Another possible difficulty with the commercialization of grafted bioflocculants could be the scale-up. Higher energy input is required for larger quantities, and relatively high equipment cost is needed if the microwave grafting method is going to be employed for the synthesis. Furthermore, there is a lack of investigations on applying grafted flocculants in the treatment of wastewaters on a consistent basis.

To address all the above-mentioned challenges, comprehensive investigation is required to prove validity and promote industrial applications of the grafted flocculants. More research is needed to derive maximum benefits of the microwave grafting technology and grafted bioflocculants in order to balance the high cost of scaling up and operation. Optimization of the grafting conditions is essential to ensure the continuous reproducibility and cost-effectiveness which are the prerequisites to meet practical quality. Furthermore, the effect of the flocculants on the environment and humans should be determined, and appropriate approvals must be obtained before they are used in water and wastewater treatment at a large scale.

4. CONCLUSIONS

Owing to the increasing demand of environmental friendly technologies in industry, utilization of natural flocculants for turbidity and contaminants removal represents an important progress in sustainable environmental technology. They are nontoxic, biodegradable, can be obtained from renewable resources and their application is directly related to the improvement of quality of life for underdeveloped communities. Several studies have been conducted to investigate the flocculating properties or behavior of plant-based bioflocculants in wastewater treatment. The results demonstrated that they are technically promising as flocculants with a high removal efficiency of solids, turbidity, color, and dye. However, its development is constrained with variation of flocculating efficiency, fast degradation, and high production cost.

Modification of natural polymers with chemical grafting has been studied recently to improve the flocculating characteristics. The developed plant-based grafted bioflocculants essentially combine the best properties of both natural and synthetic polymers and exhibit higher flocculating performance. However, the complexity of the synthesis process, the environmental issue, and safety concern of the grafting process, the extent of biodegradability, and high production cost are the current challenges to be overcome. Bridging was reported to be the responsible mechanism underlying the flocculating action of bioflocculants.

All the studies about plant-based bioflocculants took place under lab-scale conditions, and their applications in industry are still at their infancy. Therefore, possible applications of natural flocculants in different industries include food and beverage, mineral, papermaking, and oleo-chemical are suggested in this study to highlight the potential utilization of bioflocculants in diverse sectors. For the sake of ecology and human health, more qualitative and quantitative research is necessary to be carried out to further exploit the applications of plant-derived bioflocculants in different industries and to address all the issues mentioned in this work.

■ ASSOCIATED CONTENT

Supporting Information

Background of processing industries involving clarification/flocculation process. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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