



Lee, Chai Siah and Chong, Mei Fong and Robinson, John P. and Binner, Eleanor (2014) A review on development and application of plant-based bioflocculants and grafted bioflocculants. *Industrial and Engineering Chemistry Research*, 53 (48). pp. 18357-18369. ISSN 0888-5885

**Access from the University of Nottingham repository:**

<http://eprints.nottingham.ac.uk/31940/1/Revised%2520manuscript%2520of%2520review%2520paper.pdf>

**Copyright and reuse:**

The Nottingham ePrints service makes this work by researchers of the University of Nottingham available open access under the following conditions.

- Copyright and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners.
- To the extent reasonable and practicable the material made available in Nottingham ePrints has been checked for eligibility before being made available.
- Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.
- Quotations or similar reproductions must be sufficiently acknowledged.

Please see our full end user licence at:

[http://eprints.nottingham.ac.uk/end\\_user\\_agreement.pdf](http://eprints.nottingham.ac.uk/end_user_agreement.pdf)

**A note on versions:**

The version presented here may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher's version. Please see the repository url above for details on accessing the published version and note that access may require a subscription.

For more information, please contact [eprints@nottingham.ac.uk](mailto:eprints@nottingham.ac.uk)

# **A review on development and application of plant-based bio-flocculants and grafted bio-flocculants**

Chai Siah Lee<sup>a,b</sup>, Mei Fong Chong<sup>a\*</sup>, John Robinson<sup>b</sup>, Eleanor Binner<sup>b</sup>

<sup>a</sup>Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham Malaysia Campus, 43500 Semenyih, Selangor, Malaysia

<sup>b</sup>Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham NG7 2RD, UK

\* Corresponding author. Tel.: +60 3 8924 8347; fax: +60 3 8924 8017.

E-mail addresses: MeiFong.Chong@nottingham.edu.my (M.F. Chong),

enxsl@nottingham.ac.uk (C.S. Lee), enzjpr@exmail.nottingham.ac.uk (J. Robinson),

ezzeb@exmail.nottingham.ac.uk (E. Binner)

## **Abstract**

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

Keywords: plant-based bio-flocculants; grafted copolymers; flocculation; clarification; polysaccharides; biodegradable

---

### **Abbreviations**

---

COD: chemical oxygen demand

SS: suspended solids

LDS: light diffraction scattering

TDS: total dissolved solids

---

## **1. Introduction**

Flocculation is one of the important separation processes that are extensively employed in portable water, domestic or industrial wastewater treatment. Various types of flocculants have been developed and marketed for the removal of environmental concerned parameters such as suspended and dissolved solids, turbidity, chemical oxygen demand (COD), colour and dye

through sedimentation. They have been applied in diverse range of wastewaters such as food and beverages, paper manufacturing, agricultural production, dyes or textile, municipal and others.<sup>5</sup> One of the leading manufacturers of flocculants (BASF: Badische Anilin- und 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.<sup>6</sup> Through 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 which are inorganic flocculants and organic polymeric flocculants.

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

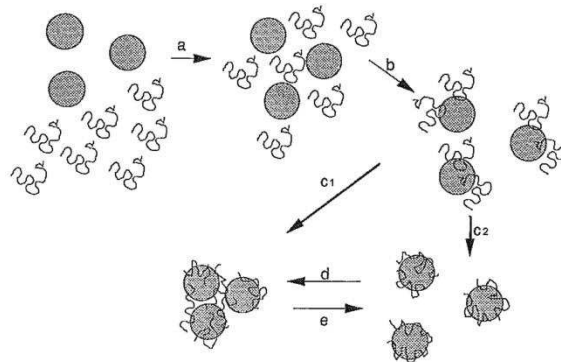


Figure 1. Action of charge neutralisation of cationic flocculant with the particle surface<sup>11</sup>

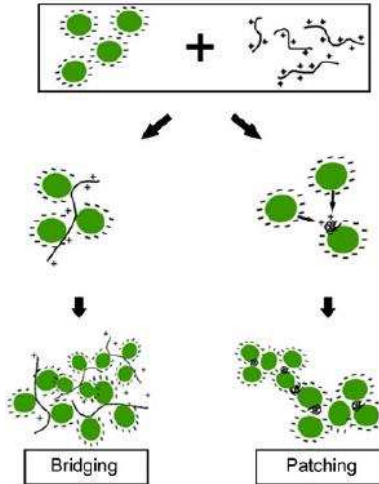


Figure 2. Flocculation mechanisms of bridging and patching<sup>12</sup>

Organic polymeric flocculants such as polyacrylamide have become very important in wastewater treatment due to its greatest advantage with remarkable ability to flocculate even when added in small quantities (ppm).<sup>7</sup> High molecular weight polymers with long 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.<sup>13</sup> Hence, the flocs formed are bigger, stronger and denser with good settling characteristics.<sup>14</sup> In addition, they are easy to handle, immediately soluble in aqueous systems, not sensitive to pH and produce lower sludge volume.<sup>10</sup> 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.<sup>10, 13, 15</sup> Sludge formed at water treatment plants with polymeric flocculants has a limited potential for recycling due to the non-biodegradability of synthetic polymers.<sup>1</sup>

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.<sup>13, 16</sup> Researchers are trying to discover high efficient and eco-friendly bio-flocculants with the aim to replace the conventional flocculants. Biopolymers based flocculants have attracted wide interest from researchers because they have the advantages of biodegradability, non-toxic and easily available from reproducible agricultural resources.<sup>10, 14, 17</sup>

Natural organic flocculants which are based on natural polymers or polysaccharides like starch, cellulose, chitosan, natural gums, mucilage and 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.<sup>10</sup> 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<sup>18, 19</sup> and papermaking industry.<sup>20</sup> Sodium carboxymethylcellulose

(CMCNa) is produced by chemical modification of cellulose and has been tested as eco-friendly flocculants for drinking water treatment.<sup>21</sup> Natural gums, such as guar gum and xanthan gum have been studied extensively as an effective flocculants over a wide range of pH and ionic strengths for treatment of wastewater from various industries.<sup>22, 23</sup>

The plant-based bio-flocculants contain natural polysaccharides which are suspected to exhibit excellent selectivity towards aromatic compounds and metals, thus efficient in the removal of pollutants from wastewater.<sup>24</sup> However, it was reported that their feasibility is restricted by moderate flocculating property and short shelf life.<sup>25</sup> In recent years, grafted bio-flocculants are developed and claimed to have remarkable flocculating ability and biodegradability. As shown in Figure 3, natural bio-polymers are covalently bonded (modified) by inclusion of synthetic monomers (e.g. acrylamide) onto their backbone to synthesise the high molecular weight grafted copolymers that exhibit improved flocculating properties.<sup>26</sup>

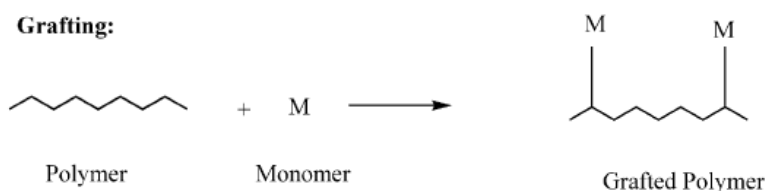


Figure 3. Schematic representation of grafting method in polymer modification<sup>27</sup>

The rising concern of environmental pollution problems and health-concerning issues causes the utilisation of bio-flocculants derived from natural sources as an important progress in sustainable environmental technology. In this review, the development and flocculating abilities of plant-based bio-flocculants and grafted bio-flocculants is reported for the first time. The preparation methods of plant-based bio-flocculants 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 bio-flocculants and grafted bio-flocculants, the current challenges and future perspectives, and the potential application of plant-based bio-flocculants in diverse industries.

## 2. Plant-based bio-flocculants

Natural plant-based bio-flocculants emerge as an attractive alternative to polymeric flocculants and their applications in wastewater treatment has become increasingly essential, in light of their biodegradability, non-toxic, widely available from renewable resources, environmental friendly processing and have no negative impact on the environment. The applications of plant-derived bio-polymers for treatment of various types of wastewater have been discovered and reported. Plant-based bio-flocculants 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.<sup>1, 3, 4, 28</sup>

## 2.1 Plant materials and bio-flocculants preparation methods

Table 1 shows six different types of plants which have been investigated of 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 mucilaginous texture with polysaccharides as the main components and they are having neutral pH in nature. Mucilage is plant hydrocolloids that have viscous 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.<sup>29-31</sup> 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.

Table 1. Plants that have been investigated of their flocculating properties

Plant species		Charge	pH	Solubility in water	Active ingredients	Extraction method	Extracted plant part	References
Scientific name	Common name							
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

There are two methods for the production of plant-derived bio-flocculants which have been reported thus far, which are (i) solvent extraction and precipitation<sup>2, 3, 33, 36-41</sup> and (ii) drying and grinding.<sup>1, 28</sup> The detailed procedures for each method are illustrated in Figure 4. The methodologies used to produce the bio-flocculants are environmental-friendly, no toxic chemical used, easy and simple. As listed in Table 1, the solvent extraction and precipitation method has been applied for extraction of bio-flocculants 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 has been used for preparation of bio-flocculants from Mallow, Okra, and Isabgol. The cleaned materials were dried at high temperature, and then grounded and sieved to obtain the bio-flocculants. It was discovered that the bio-flocculants obtained had lower flocculating activity. Low removal efficiency of COD, color and suspended solids (SS) at 17, 27 and 41% respectively

was reported when it was used as flocculant in treatment of landfill leachate with direct flocculation process.<sup>28</sup> They were found to be more effective in coagulation-flocculation process where coagulant was added before bio-flocculant. On the other hand, the bio-flocculants that are prepared with solvent extraction and precipitation displayed excellent flocculating ability in the treatment of wastewater with direct flocculation process where no coagulant and pH adjustment are required. This finding indicated that extraction step is closely related with flocculating efficiency and plays the major role to extract the active constituents with high flocculating activity from the plant materials.

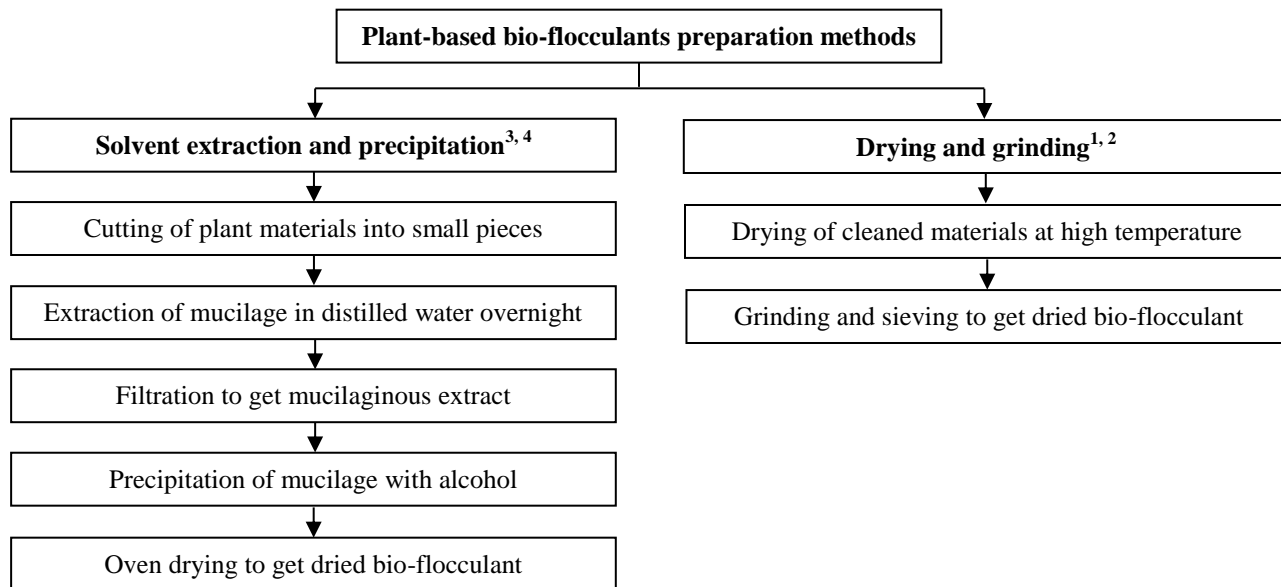


Figure 4. Preparation methods of plant-based bio-flocculants

Up to date, all the studies that investigated the flocculating property of bio-flocculants only paid attention to the flocculation process and analysed the effects of flocculant dose, contact time and pH on the flocculation efficiency.<sup>2, 3, 40</sup> 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 optimise the extraction conditions in order to produce the most efficient bio-flocculants that are comparable to commercial flocculants in terms of cost and flocculating efficiency.

## 2.2 Flocculation efficiency

Jar test<sup>42</sup> is used to evaluate the flocculating abilities of the plant-based bio-flocculants and optimise the flocculation process in most studies. The identified usage of natural flocculants and their technical viability for industrial wastewater are currently limited to only academic research. Their flocculating performance reported in literature has been compiled and summarised 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.<sup>33, 40</sup> Fenugreek<sup>40</sup> and Okra<sup>33</sup> mucilage were proven to be as effective as commercial flocculant (polyacrylamide) in treatment of tannery effluent and sewage wastewater.

Table 2. Flocculating efficiencies of plant-based bio-flocculants

Plant-based bio-flocculants and its preparation method	Treated wastewater	Sedimentation period (minutes)	Optimum pH	Optimum coagulant dose (mg/L)	Optimum bio-flocculant dose (mg/L)	Flocculation efficiency		Reference
						Types of removal	% removal	
Isabgol (drying and grinding)	Semi-aerobic landfill leachate	120	6.5 to 7.5	7200	400	COD	64	28
						Colour	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
	Sewage and tannery	60	7	-	1.2	TDS	68.76	38
					SS	94.69 and 87.03		
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
	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
	Sewage	60	4	-	0.12	SS	86.86	33
						TDS	>95	
Okra and Fenugreek (extraction and precipitation)	Textile	60	9.2	-	0.8 and 0.04	SS	98 and 94.2	43
						TDS	31.6 and 43.7	
						Colour	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	

As reported in the previous section, bio-flocculants obtained with drying and grinding exhibit lower flocculating efficiency. These bio-flocculants must be coupled with usage of coagulant in coagulation-flocculation process. Table 2 shows that the Isabgol husk prepared with drying and grinding was effective as coagulant aid for the treatment of landfill leachate with poly-aluminium chloride (PACl) as the coagulant.<sup>28</sup> 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 grinded mallow and okra bio-flocculants were efficient in removing turbidity from synthetic kaolin suspension and biologically-treated effluent when aluminium sulphate was used as the coagulant.<sup>1</sup> On the other hand, the bio-flocculants extracted with water as the solvent display remarkable flocculating performance in direct flocculation process. High removal efficiency of solids either in suspended (SS) or dissolved forms (TDS), dye, turbidity and colour was achieved by using low concentration of bio-flocculant dosage. For instance, 95% removal of SS in treatment of tannery wastewater<sup>36</sup> and >95% removal of TDS in treatment of sewage effluent<sup>33</sup> were attained with 0.04 mg/L and 0.12 mg/L of okra bio-flocculant. Mallow and okra bio-flocculants were reported to have high efficiency in turbidity removal at 97% in treatment of synthetic (kaolin) wastewater.<sup>1</sup> In other paper, dye removal as

high as 71%<sup>3</sup> and colour removal at 53%<sup>43</sup> were achieved by using psyllium and okra bio-flocculants respectively.

As shown in Table 2, long sedimentation period (60 and 120 minutes) was reported in some literature. It is postulated that the flocs formed are weaker and smaller in size and thus longer settling time is required. In the study of *Tamarindus indica* (Tamarind) as bio-flocculant, 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.<sup>4</sup> In most of the reported studies, the suitable pH range was neutral for maximum flocculating efficiency of bio-flocculants. 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 neutralisation, electrostatic patch and polymer bridging.<sup>13</sup> The flocculation mechanism of charge neutralisation is only applicable when the colloid suspended particles and the added flocculants are of opposite charge.<sup>13</sup> In many cases, impurity particles are negatively charged. As shown in Table 1, the ionic charges of bio-flocculants are anionic for Okra, Psyllium and Isabgol, neutral for Fenugreek and unknown for Mallow and Tamarind. Since most of the bio-flocculants are verified to be either anionic or neutral, it is presumed that charge neutralisation is not the responsible mechanism. Thus, the most probable mechanism that happened between plant-derived bio-flocculants with particulate matter in effluent is polymer bridging where the bio-polymers serve as a bridge based on particle-polymer-particle complex formation. The bridging mechanism involved in bio-flocculation as shown in Figure 5 has been reported in a study by using one flocculating microalgae to concentrate the non-flocculating microalgae of interest.<sup>12</sup>

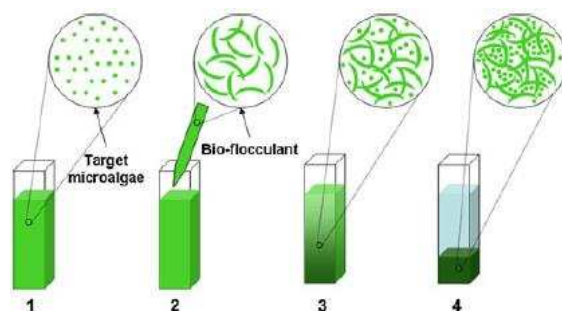


Figure 5. Bridging mechanism in bio-flocculation of microalgae<sup>12</sup>

In order to be effective in destabilisation, a bio-polymer molecule must contain chemical groups (free hydroxyl group), which is the possible binding sites that can interact with sites on the surface of the colloidal particles. When a bio-polymer 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 bio-polymer serves as a bridge.<sup>41</sup> Polymer bridging has been proposed as the plausible mechanism for flocculation behaviour in treatment of textile wastewater with *Plantago psyllium* mucilage<sup>3</sup> and *Tamarindus indica* mucilage.<sup>4</sup> For other bio-flocculants, 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.<sup>2, 33, 38-40</sup> 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,<sup>2, 33, 38-40</sup> 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 is primarily depend on the electrical properties, 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.<sup>28</sup> Through measurement of zeta potential, the ionic charge of the bio-flocculants and the surface charge of the suspended particles could 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 used as a tool to evaluate different types of flocculation mechanism depending on the flocculants characteristics.<sup>44, 45</sup> It 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, by combining the measurement of zeta potential and LDS technique, performance of the bio-flocculants during flocculation could be monitored. The flocculation kinetics and mechanism of the bio-flocculants could then be determined.

## **2.4 Current challenges and future perspectives**

Even though most of the studies have proven that the bio-flocculants were workable and effective for treatment of various types of wastewaters, all these research were carried out in laboratory scale and only tested in treatment of wastewaters. There are many factors that restrict its development and application in industry. The four major problems including sensitivity of bio-products 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 great extent.<sup>46</sup> In addition, the chemical composition and molecular structure of hydrocolloids often depend on the source, extraction methods and any further processing conditions.<sup>30</sup> For instance, the rheological properties and viscoelastic behaviour of natural plant gums depend on the method and condition of extraction, purification, drying and further modification processes.<sup>47</sup> Thus, more investigation concerning the processing methods and conditions (preparation, extraction, purification, drying and storage)

of bio-flocculants is strongly important because it will determine the quality and stability of bio-flocculants.

Bio-polymers face degradation of products with time and processing parameters or conditions.<sup>29</sup> 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.<sup>48</sup> In addition, the flocs tend to lose stability and strength with time because of their biodegradability.<sup>49</sup> Materials with reduced moisture content will resist germination under favourable conditions, thus prolonging the storage life. Therefore, drying process is of vital importance to produce high quality bio-flocculants where 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 due to their relatively lower molecular weight and shorter shelf life.<sup>25</sup> Hence, optimisation study of processing, extraction and drying conditions is highly important to get the optimum conditions that can produce the bio-flocculants with maximum yield and flocculating ability.

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

Nonetheless, the future development of cost-effective and environmental-friendly plant based bio-flocculants 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 related to bio-flocculants should continue and in-line with environment and health protection.

## **2.5 Possible application of plant-based bio-flocculants in different industries**

To date, there is no detailed study about the applicability or feasibility of plant-derived bio-flocculants in other industries apart from wastewater treatment. Their application studies are only at preliminary level and conducted on 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 clarification or flocculation process in the manufacturing of certain products. The clarification or flocculation method or agent used in different industries are summarised in Table 3.

Table 3. Clarification/flocculation process in different industries

Application area	Separated components	Clarification/flocculation method/agent	References	
Beverage industry	Clarification of wine	Iron compounds, suspended solids, proteins, dead yeast cells	Activated carbon, gelatin, albumen, bentonite	50-53
	Clarification of vinegar	Iron compounds, suspended solids, proteins	Activated carbon, gelatin, albumen	50, 51
	Clarification of fruit juices	Suspended particles, proteins, polyphenols, pectins, carbohydrates	Gelatin, bentonite, kieselsol, silica sol, polyvinylpyrrolidone (PVPP) or combination of these compounds, chitosan	54-58
	Clarification of dates extract	Non-soluble matter, colouring matter and semi-soluble (e.g. pectin) material	Activated carbon, bentonite, PVPP	59, 60
	Clarification of sugar cane juice	Organic and inorganic constituents, suspended solids	Lime, bentonite, activated carbon, polyacrylamide polymer	61-64
Food industry	Recovery of muscle proteins from fish processing by-products	Bones, scales, skin, fats	Isoelectric solubilisation/precipitation, polymeric flocculants (anionic, non-ionic and cationic)	65, 66
	Recovery of muscle proteins from meat processing by-products	Bones, scales, skin, fats	Isoelectric solubilisation/precipitation, mechanical deboning	67-69
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)	70-72
Paper industry	Retention of fine matters during papermaking	Cellulose fines, fibre fines and fillers	Polyelectrolytes flocculants (e.g. polyacrylamides, poly-aluminium chloride, polyethylene oxide), modified starches, chitosan	20, 44, 73-77
Oleo-chemical or biodiesel industry	Clarification of crude glycerol	Methanol, inorganic salt (catalyst residue), free fatty acids, lipids, unreacted mono- or di- or triglycerides, non-glycerol organic matters	Chemical treatments, physical treatments (gravitational settling, centrifugation, evaporation, distillation), micro and ultra-filtration	78-83

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 much preferred and will be the primary concern in many industries. Many of the conventional clarification and flocculation methods listed in Table 3 have its 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 bio-flocculants 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 bio-flocculants could be a suitable alternative to the current flocculation/clarification methods in food and beverage, mineral, paper-making, oleo-chemical and biodiesel industries are attached in Supporting Information.

Plant-based bio-flocculants have been proven to remove impurities, turbidity, organic and inorganic loads, suspended and dissolved solids effectively. Besides, natural water-soluble polysaccharides have the capability of flocculating small particles.<sup>38</sup> The long chain of polysaccharides has the ability to bind or bridge different components and result in efficient removal of undesirable compounds. Okra,<sup>36</sup> Fenugreek<sup>40</sup> and Psyllium<sup>38</sup> bio-flocculants 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, fibres and toxic pollutants from textile and sewage wastewaters.<sup>2, 39</sup> Thus, they may exhibit the capability to clarify the juices extract, flocculate and recover the muscle proteins from seafood and meat processing by-products and improve the retention of fibres and fillers in papermaking industry.

A study showed that okra and mallow bio-flocculants exhibited the flocculating ability to remove the turbidity from kaolin suspension solution effectively.<sup>1</sup> Therefore, plant-based bio-flocculant 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 cosmetic and pharmaceutical industry.

In oleo-chemical industry, the use of natural bio-flocculants is postulated to have the advantages of 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 bio-flocculants, strong and dense flocs could be formed in short time. After sedimentation, the formed flocs are easily separated through sedimentation. Since no chemical is used in the purification process, the purified glycerol could be applied safely for a range of application in pharmaceutical or cosmetic industries. It is predicted that the bio-flocculants may consists 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 bio-flocculants**

In recent years, chemical modification of natural macromolecules, especially polysaccharides, has received considerable interest to improve their flocculating properties.<sup>84, 85</sup> Such modification is done to overcome the drawbacks in term of moderate flocculation performance, uncontrolled biodegradability, and varying efficiency due to different processing conditions.<sup>86</sup> The biodegradability of natural polysaccharides needs to be suitably controlled<sup>87</sup> 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 non-biodegradable and toxic to environment.<sup>17, 88</sup> The improvement in the properties of natural and synthetic polymers can be performed by developing grafted copolymers.<sup>89</sup>

Graft copolymerisation is aimed to obtain 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 polymers branches onto the rigid backbone of natural ones.<sup>89</sup> 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.<sup>90, 91</sup> Recently, the common polymers such as polyacrylamide have been grafted onto the backbone of plant-based bio-polymers (*Plantago ovata*, *Plantago psyllium* and *Tamarindus indica*) and showed significant improved flocculating properties compared to ungrafted natural polysaccharides.<sup>92-94</sup> The flocculating performance of all the plant-based grafted bio-flocculants reported in literature is summarised in Table 4.

Table 4. Flocculating efficiencies of plant-based grafted bio-flocculants

Plant-based grafted bio-flocculant	Grafting method	Treated wastewater	Sedimentation time	Optimum dose (ppm)	Flocculation efficiency		Reference
					Type of removal	Results	
Polyacrylamide-grafted-Plantago psyllium (Psy-g-PAM)	Conventional free radical	Tannery and domestic wastewater	1hour	60	SS	>95% and >89%	94
		Textile wastewater	1hour	1.6	SS	>93%	95
						TDS	72%
Polyacrylonitrile-grafted-Plantago psyllium (Psy-g-PAN)	Conventional free radical	Textile effluent	1hour	1.6	SS	94%	96
		Tannery effluent	1hour	1.2	SS	89%	88
						TDS	27%
Polymethacrylic acid-grafted-Plantago psyllium (Psy-g-PMA)	Microwave-assisted	Municipal sewage wastewater	25min	2.5	Turbidity	100 to 12NTU	97
Polyacrylamide-grafted-Plantago ovata	Microwave-initiated	0.25% kaolin suspension	15 min	0.75	Turbidity	59 to 22NTU	93
		1% coal fine suspension			OD	1.5 to 0.25	
Polymethylmethacrylate-grafted-Plantago ovata	Microwave-assisted	0.25% kaolin suspension	15 min	1	Turbidity	185 to 70NTU	98
Polyacrylamide-grafted-Tamarindus indica (Tam-g-PAM)	Conventional free radical	Textile wastewater	10min	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	15min	0.5	Turbidity	125 to 6NTU	99, 100
		Municipal sewage and textile industry wastewaters		9	Turbidity	58 to 14NTU and 97 to 80NTU	
					SS	335 to 55ppm and 295 to 50ppm	
					TDS	265 to 205ppm and 345 to 295ppm	
Hydrolysed polyacrylamide-grafted-Tamarind kernel polysaccharide (Hyd. TKP-g-PAM)	Microwave-assisted	Kaolin suspension	15min	0.5	Turbidity	125 to 6NTU	92
		Municipal sewage wastewater		9	Turbidity	58 to 6NTU	
					SS	335 to 20ppm	
					TDS	265 to 190ppm	
				COD	540 to 295ppm		
				COD	540 to 155ppm		

### 3.1 Grafting methods

Grafted copolymers consist of a long sequence of one polymer with one or more branches of another polymer.<sup>101</sup> With the help of preformed polymer (polysaccharide in 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 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.<sup>85, 102</sup> Conventional redox, microwave-initiated and microwave-assisted grafting methods have been reported to have successfully synthesised plant-based grafted bio-flocculants.<sup>93, 98-100</sup> 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 conventional, microwave-initiated and microwave-assisted method.<sup>100</sup>

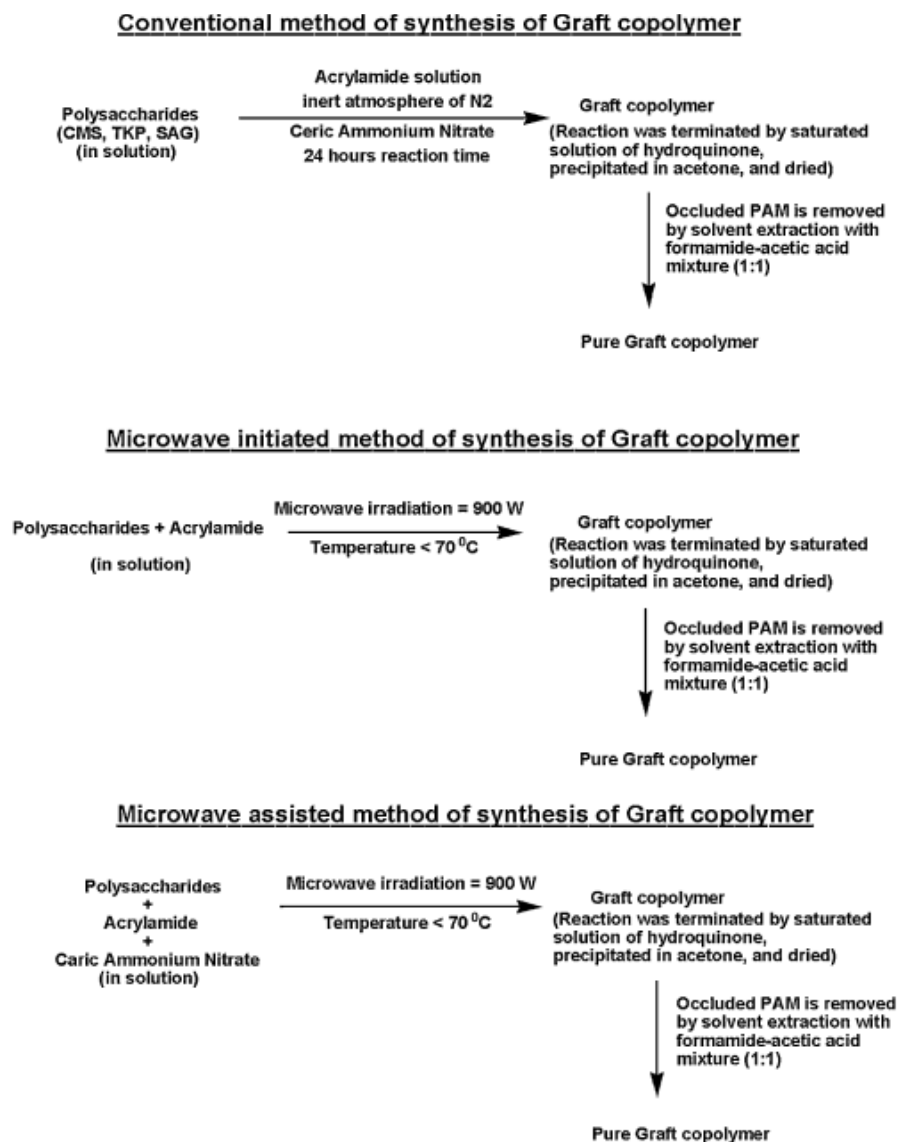


Figure 6. Schematic representation for the synthesis of grafted copolymers using conventional, microwave-initiated and microwave-assisted method<sup>100</sup>

Conventional redox (or conventional free radical) grafting method using chemical free radical initiators (e.g. ceric ammonium nitrate (CAN))<sup>41, 88, 94-96</sup> with nitrogen as the inert gas is commonly used to synthesise grafted copolymers. However, 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 problem in the commercialisation of the grafting procedures.<sup>84</sup> 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.<sup>100, 103</sup> 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.<sup>25, 84</sup> It may be used along with a chemical free radical initiator (microwave assisted technique)<sup>90, 104</sup> or even without any chemical free radical initiator (microwave initiated technique).<sup>105</sup> Microwave based techniques have certain advantages over other conventionally used techniques for free radical generation. It is reliable, easy to operate and highly reproducible. Hence, they offer a promising breakthrough for synthesis of grafted copolymers and encourage their further utilisation in various applications.<sup>84, 85</sup> As listed in Table 3, plant-based grafted bio-flocculants have been successfully synthesised with microwave-assisted and microwave-initiated techniques by using acrylamide or methacrylic acid as the monomers.<sup>92, 93, 97, 99, 100</sup> Grafted bio-flocculants synthesised by microwave initiated and microwave assisted methods were proved to provide a better quality grafted copolymers with higher percentage of grafting in comparison with conventional redox grafting method.<sup>99, 100</sup> Some research findings showed that the grafted copolymers synthesised by microwave-assisted method presented superior flocculation characteristics when compared with grafted flocculants synthesised by conventional and microwave initiated methods as well as with commercially available non-ionic flocculant (Rishfloc 226 LV).<sup>99, 100</sup>

Even though grafted bio-flocculants synthesised with microwave technology present superior flocculating characteristics but 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.<sup>84</sup> Their use is not encouraged due to 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 it is associated with high equipment cost which would increase the production cost of the copolymers and severely limit the application of grafted bio-flocculants 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 minimise the competing homopolymer formation and also to prevent formation of unwanted vapours, which may be toxic/carcinogenic due to presence of acrylamide.<sup>93</sup>

### **3.2 Flocculation efficiency**

As shown in Table 4, plant-based grafted bio-flocculants have been successfully synthesised and applied in treatment of various types of wastewaters or effluents, and resulted in higher decrease in the 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,<sup>96</sup> polymethacrylic acid,<sup>97</sup> polymethylmethacrylate<sup>98</sup> were successfully used in production of grafted bio-flocculants with high removal capability in solids and turbidity.

As expected, the grafted bio-flocculants 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<sup>93</sup> which leads to higher flocculation efficacy.<sup>106</sup> For example, *Plantago psyllium* mucilage grafted polyacrylamide (Psy-g-PAM) copolymer was proved to be a better flocculant than pure *Psyllium* mucilage in the treatment of tannery and domestic wastewater.<sup>94</sup> 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.<sup>41</sup> Another study reported that polyacrylamide grafted tamarind kernel polysaccharide (TKP-g-PAM) synthesised by microwave-assisted grafting method was superior to TKP and polyacrylamide-based commercial flocculant (Rishfloc 226 LV) in flocculation tests.<sup>99</sup>

In a study, hydrolysed polyacrylamide-grafted tamarind kernel polysaccharide (Hyd. TKP-g-PAM)<sup>92</sup> was synthesised 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.<sup>107</sup> These properties result in a higher radius of gyration as well as pervaded volume and hence a higher flocculation efficiency obtained.<sup>106</sup>

The flocculating efficiency of grafted bio-flocculants obtained with different grafting methods is compared in some studies. In a research work, the flocculation performance of the optimised grade of grafted copolymers (TKP-g-PAM) synthesised by microwave assisted method showed the best flocculation efficiency followed by optimised grafted copolymers synthesised by microwave initiated method and lastly free radical initiated grafting method in the treatment of synthetic wastewater (kaolin suspensions) and municipal sewage wastewater.<sup>100</sup> Another study<sup>99</sup> 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 bio-flocculant synthesised with conventional method.

As a concluding remark, grafted copolymers synthesised by microwave initiated and assisted method display better flocculation efficiency with higher percentage of grafting compared to conventional redox grafting method.<sup>100</sup> The higher the percentage of grafting, the longer the grafted chains with higher molecular weight and radius of gyration could be obtained. With increase in molecular weight and radius of gyration, the approachability of the contaminants towards the grafted copolymers will be increased and as the results better flocculation efficiency could be achieved.<sup>106, 108</sup>

### **3.3 Flocculation mechanism**

For grafted bio-flocculants, it was reported that the increased in flocculation efficiency was contributed by increased in chain length and molecular weight.<sup>94</sup> Polyacrylamide grafted polysaccharides are mainly non-ionic or anionic in nature<sup>92</sup> 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 bio-flocculant is essentially because of polymer bridging mechanism, because the segments of a polymer chain can adsorb onto different particles surface and form bridges between adjacent particles. As the grafted bio-flocculants exhibit the characteristics of long polymer chains (high molecular weight) and high radius of gyration, hence the adsorbed polymer molecules tend to adopt more extended configuration for interacting with more than one particle and lead to effective formation of particle-polymer-particle complex (flocs).<sup>87, 109</sup>

As reported in a study,<sup>99</sup> polymer bridging was responsible for better flocculating property of the grafted copolymers over linear polymer where the segments of a polymer chain were adsorbed onto different particles, thus linking the particles together. Some studies<sup>94, 95</sup> 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 bio-flocculant 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 behaviour of the flocculation curve was reported to be corresponded with the bridging mechanism involved behind the phenomenon.<sup>88, 93</sup> Another study stated that due to the flexible polyacrylamide graft chains, the colloidal particles aggregate through bridging effect and form larger net-like flocs. Then, with the help of enhanced approachability of polyacrylamide chains, the larger flocs with net-like structure can further seize residual particles from water through sweeping effect.<sup>110</sup> Finally, the compacted flocs are formed and settle down.

Most of the reported studies in this field are focused mainly in application of grafted bio-flocculants in wastewater treatment. The investigation of its 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 bio-flocculants, it is proposed that measurement of molecular weight and observation of flocs formation with dynamic light scattering techniques for ungrafted and grafted bio-flocculants could be applied to identify the responsible flocculation mechanism.

### **3.4 Current challenges and future direction**

The on-going research on plant-based grafted bio-flocculants is conducted on laboratory scale in treatment of wastewaters or effluents. There are many factors that constraint 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 bio-flocculants in 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.<sup>111</sup> For acrylonitrile, studies showed that it is a mutagen, a tetragen and a carcinogen.<sup>103</sup> This factor would limit its application in those industries that produce human consumed products.

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

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

In order to address all the above mentioned challenges, comprehensive investigation is required to prove their validity and promote their industrial applications. More research is needed to derive maximum benefits of microwave grafting technology and grafted bio-flocculants in order to balance the high cost of scaling up and operation. Optimisation of the grafting conditions is essential to ensure the continuous reproducibility and cost-effectiveness which are the prerequisite to meet practical quality. Furthermore, the effect of the flocculants to the environment and human should be determined and appropriate approvals obtained before it is used in water and wastewater treatment in large scale.

#### **4. Conclusions**

Due to the increasing demand of environmental friendly technologies in industry, utilisation 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 behaviour of plant-based bio-flocculants in wastewater treatment. The results demonstrated that they are technically promising as flocculants with high removal efficiency of solids, turbidity, colour 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 bio-flocculants 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 bio-flocculants.

All the studies about plant-based bio-flocculants 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 including food and beverage, mineral, papermaking and oleo-

chemical are suggested in this study to highlight the potential utilisation of bio-flocculants in diverse sectors. For the sake of ecology and human health, more qualitative and quantitative research are necessary to be carried out to further exploit the applications of plant-derived bio-flocculants in different industries and to address all the issues mentioned above.

### Associated Content

Supporting Information Available: Background of processing industries involving clarification/flocculation process. This material is available free of charge via the internet at <http://pubs.acs.org>.

### References

- (1) Anastasakis, K.; Kalderis, D.; Diamadopoulos, E., Flocculation behavior of mallow and okra mucilage in treating wastewater. *Desalination* **2009**, 249, (2), 786-791.
- (2) Mishra, A.; Srinivasan, R.; Dubey, R., Flocculation of Textile Wastewater by Plantago psyllium Mucilage. *Macromolecular Materials and Engineering* **2002**, 287, (9), 592-596.
- (3) Mishra, A.; Bajpai, M., Flocculation behaviour of model textile wastewater treated with a food grade polysaccharide. *Journal of Hazardous Materials* **2005**, 118, (1-3), 213-217.
- (4) Mishra, A.; Bajpai, M., The flocculation performance of Tamarindus mucilage in relation to removal of vat and direct dyes. *Bioresource Technology* **2006**, 97, (8), 1055-1059.
- (5) Lee, C. S.; Robinson, J.; Chong, M. F., A review on application of flocculants in wastewater treatment. *Process Safety and Environmental Protection* **2014**, In Press.
- (6) Weigert, H. Water Solutions. <http://www.basf.com/group/corporate/chemistryworldtour/en/innovationen/zetag-9000> (accessed Nov 5, 2014).
- (7) Sharma, B. R.; Dhuldhoya, N. C.; Merchant, U. C., Flocculants—an Ecofriendly Approach. *Journal of Polymers and the Environment* **2006**, 14, (2), 195-202.
- (8) Chong, M., Direct Flocculation Process for Wastewater Treatment. In *Advances in Water Treatment and Pollution Prevention*, Sharma, S. K.; Sanghi, R., Eds. Springer Netherlands: 2012; pp 201-230.
- (9) Ahmad, A. L.; Wong, S. S.; Teng, T. T.; Zuhairi, A., Improvement of alum and PACl coagulation by polyacrylamides (PAMs) for the treatment of pulp and paper mill wastewater. *Chemical Engineering Journal* **2008**, 137, (3), 510-517.
- (10) Renault, F.; Sancey, B.; Badot, P. M.; Crini, G., Chitosan for coagulation/flocculation processes – An eco-friendly approach. *European Polymer Journal* **2009**, 45, (5), 1337-1348.
- (11) Bizi, M., Stability and flocculation of nanosilica by conventional organic polymer. *Natural Science* **2012**, 4, (6), 372-385.
- (12) Salim, S.; Bosma, R.; Vermuë, M.; Wijffels, R., Harvesting of microalgae by bio-flocculation. *Journal of Applied Phycology* **2011**, 23, (5), 849-855.
- (13) Bolto, B.; Gregory, J., Organic polyelectrolytes in water treatment. *Water Research* **2007**, 41, (11), 2301-2324.
- (14) Singh, R. P.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Pandey, S. R.; Tripathy, T.; Panda, J.; Kanan, K.; Jain, S. K.; Lan, N. T., Biodegradable drag reducing agents and flocculants based on polysaccharides: Materials and applications. *Polymer Engineering & Science* **2000**, 40, (1), 46-60.
- (15) Young-Han Bae, H.-J. K., Eun-Joo Lee, Nak-Chang Sung, Sung-Sik Lee, and Young-Han Kim, Potable water treatment by polyacrylamide base flocculants, coupled with an inorganic coagulant. *Environmental Engineering Research* **2007**, 12, (1), 21-29.
- (16) Lu, L.; Pan, Z.; Hao, N.; Peng, W., A novel acrylamide-free flocculant and its application for sludge dewatering. *Water Research* **2014**, 57, (0), 304-312.

- (17) Pal, S.; Mal, D.; Singh, R. P., Cationic starch: an effective flocculating agent. *Carbohydrate Polymers* **2005**, 59, (4), 417-423.
- (18) Zhang K, Z. Q., Wu W., Wastewater treatment efficiency of combined aluminum-starch flocculant. *The Journal of Applied Ecology* **2004**, 15, (8), 1443-1446.
- (19) XING Guo-xiu, Z. S.-f., JU Ben-zhi, YANG Jin-zong, Recent Advances in Modified Starch as Flocculant. *The Proceedings of the 3rd International Conference on Functional Molecules* **2005**.
- (20) Michele M. Merrette, J. J. T., Paul H. Richardson STARCHES FOR USE IN PAPERMAKING. U.S. Patent US 6,843,888 B2, Jan 18, 2005.
- (21) Khiari, R.; Dridi-Dhaouadi, S.; Aguir, C.; Mhenni, M. F., Experimental evaluation of eco-friendly flocculants prepared from date palm rachis. *Journal of Environmental Sciences* **2010**, 22, (10), 1539-1543.
- (22) De, T. T. a. B. R., Flocculation : A New Way to Treat the Waste Water. *Journal of Physical Sciences* **2006**, 10, 93-127.
- (23) Gupta, B.; Ako, J., Application of guar gum as a flocculant aid in food processing and potable water treatment. *European Food Research and Technology* **2005**, 221, (6), 746-751.
- (24) Crini, G., Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science* **2005**, 30, (1), 38-70.
- (25) Mishra, S.; Usha Rani, G.; Sen, G., Microwave initiated synthesis and application of polyacrylic acid grafted carboxymethyl cellulose. *Carbohydrate Polymers* **2012**, 87, (3), 2255-2262.
- (26) Lee, K. E.; Morad, N.; Teng, T. T.; Poh, B. T., Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review. *Chemical Engineering Journal* **2012**, 203, (0), 370-386.
- (27) Bhattacharya, A.; Misra, B. N., Grafting: a versatile means to modify polymers: Techniques, factors and applications. *Progress in Polymer Science* **2004**, 29, (8), 767-814.
- (28) Al-Hamadani, Y. A. J.; Yusoff, M. S.; Umar, M.; Bashir, M. J. K.; Adlan, M. N., Application of psyllium husk as coagulant and coagulant aid in semi-aerobic landfill leachate treatment. *Journal of Hazardous Materials* **2011**, 190, (1-3), 582-587.
- (29) Jani, G. K.; Shah, D. P.; Prajapatia, V. D.; Jain, V. C., Gums and mucilages: Versatile excipients for pharmaceutical formulations. *Asian Journal of Pharmaceutical Sciences* **2009**, 4, (5), 309-323.
- (30) Mirhosseini, H.; Amid, B. T., A review study on chemical composition and molecular structure of newly plant gum exudates and seed gums. *Food Research International* **2012**, 46, (1), 387-398.
- (31) S., B. R. N. A. F. K., ISOLATION AND CHARACTERIZATION OF MUCILAGE FROM SOME SELECTED SPECIES OF ABELMOSCHUS MEDIK. (MALVACEAE) AND THEIR APPLICATION IN PHARMACEUTICAL SUSPENSION PREPARATION. *International Journal of Pharmacy and Pharmaceutical Sciences* **2013**, 5, (1), 398-402.
- (32) Ameena, K.; Dilip, C.; Saraswathi, R.; Krishnan, P. N.; Sankar, C.; Simi, S. P., Isolation of the mucilages from Hibiscus rosasinensis linn. and Okra (Abelmoschus esculentus linn.) and studies of the binding effects of the mucilages. *Asian Pacific Journal of Tropical Medicine* **2010**, 3, (7), 539-543.
- (33) Agarwal, M.; Srinivasan, R.; Mishra, A., Study on Flocculation Efficiency of Okra Gum in Sewage Waste Water. *Macromolecular Materials and Engineering* **2001**, 286, (9), 560-563.
- (34) Hirose, K.; Endo, K.; Hasegawa, K., A convenient synthesis of lepidimoides from okra mucilage and its growth-promoting activity in hypocotyls. *Carbohydrate Research* **2004**, 339, (1), 9-19.
- (35) Sengkhampan, N.; Verhoef, R.; Schols, H. A.; Sajjaanantakul, T.; Voragen, A. G. J., Characterisation of cell wall polysaccharides from okra (Abelmoschus esculentus (L.) Moench). *Carbohydrate Research* **2009**, 344, (14), 1824-1832.
- (36) Agarwal, M.; Rajani, S.; Mishra, A.; Rai, J. S. P., UTILIZATION OF OKRA GUM FOR TREATMENT OF TANNERY EFFLUENT. *International Journal of Polymeric Materials and Polymeric Biomaterials* **2003**, 52, (11-12), 1049-1057.
- (37) Srinivasan, R.; Mishra, A., OKRA (HIBISCUS ESCULENTUS) AND FENUGREEK (TRIGONELLA FOENUM GRACEUM) MUCILAGE: CHARACTERIZATION AND APPLICATION AS FLOCCULANTS FOR TEXTILE EFFLUENT TREATMENTS. *Chinese Journal of Polymer Science* **2008**, 26, (06), 679-687.

- (38) A. Mishra, M. A., M. Bajpai, S. Rajani and R.P. Mishra, Plantago psyllium mucilage for sewage and tannery effluent treatment. *Iranian Polymer Journal* **2002**, 11, (6), 381-386.
- (39) Mishra, A.; Agarwal, M.; Yadav, A., Fenugreek mucilage as a flocculating agent for sewage treatment. *Colloid and Polymer Science* **2003**, 281, (2), 164-167.
- (40) Mishra, A.; Yadav, A.; Agarwal, M.; Bajpai, M., Fenugreek mucilage for solid removal from tannery effluent. *Reactive and Functional Polymers* **2004**, 59, (1), 99-104.
- (41) Mishra, A.; Bajpai, M.; Pal, S.; Agrawal, M.; Pandey, S., Tamarindus indica mucilage and its acrylamide-grafted copolymer as flocculants for removal of dyes. *Colloid and Polymer Science* **2006**, 285, (2), 161-168.
- (42) Ives, K. J., The Scientific Basis of Flocculation. In IV ed.; Springer: Netherlands, 1978; Vol. 27, p 369.
- (43) Mishra, A.; Srinivasan, R., OKRA (HIBISCUS ESCULENTUS) AND FENUGREEK (TRIGONELLA FOENUM GRACEUM) MUCILAGE: CHARACTERIZATION AND APPLICATION AS FLOCCULANTS FOR TEXTILE EFFLUENT TREATMENTS. *Chinese Journal of Polymer Science* **2008**, 26, (06), 679-687.
- (44) Rasteiro, M. G.; Garcia, F. A. P.; del Mar Pérez, M., Applying LDS to Monitor Flocculation in Papermaking. *Particulate Science and Technology* **2007**, 25, (3), 303-308.
- (45) Rasteiro, M. G.; Garcia, F. A. P.; Ferreira, P.; Blanco, A.; Negro, C.; Antunes, E., The use of LDS as a tool to evaluate flocculation mechanisms. *Chemical Engineering and Processing: Process Intensification* **2008**, 47, (8), 1323-1332.
- (46) Jaya, S.; Durance, T. D., Compressive characteristics of cellular solids produced using vacuum-microwave, freeze, vacuum and hot air dehydration methods. *Journal of Porous Materials* **2009**, 16, (1), 47-58.
- (47) Amid, B. T.; Mirhosseini, H., Influence of different purification and drying methods on rheological properties and viscoelastic behaviour of durian seed gum. *Carbohydrate Polymers* **2012**, 90, (1), 452-461.
- (48) León-Martínez, F. M.; Rodríguez-Ramírez, J.; Medina-Torres, L. L.; Méndez Lagunas, L. L.; Bernad-Bernad, M. J., Effects of drying conditions on the rheological properties of reconstituted mucilage solutions (*Opuntia ficus-indica*). *Carbohydrate Polymers* **2011**, 84, (1), 439-445.
- (49) Pal, S.; Ghosh, S.; Sen, G.; Jha, U.; Singh, R. P., Cationic tamarind kernel polysaccharide (Cat TKP): A novel polymeric flocculant for the treatment of textile industry wastewater. *International Journal of Biological Macromolecules* **2009**, 45, (5), 518-523.
- (50) Saywell, L. G. Wine and vinegar clarification process. U.S. Patent US2043713 A, Jun 9, 1936.
- (51) Saywell, L. G., Clarification of Wine. *Industrial & Engineering Chemistry* **1934**, 26, (9), 981-982.
- (52) Catarino, S.; Madeira, M.; Monteiro, F.; Rocha, F.; Curvelo-Garcia, A. S.; de Sousa, R. B., Effect of Bentonite Characteristics on the Elemental Composition of Wine. *Journal of Agricultural and Food Chemistry* **2007**, 56, (1), 158-165.
- (53) Lambri, M.; Dordoni, R.; Silva, A.; De Faveri, D. M., Comparing the impact of bentonite addition for both must clarification and wine fining on the chemical profile of wine from Chambave Muscat grapes. *International Journal of Food Science & Technology* **2012**, 47, (1), 1-12.
- (54) Turfan, Ö.; Türkyılmaz, M.; Yemiş, O.; Özkan, M., Anthocyanin and colour changes during processing of pomegranate (*Punica granatum L.*, cv. Hicaznar) juice from sacs and whole fruit. *Food Chemistry* **2011**, 129, (4), 1644-1651.
- (55) Siebert, K. J.; Lynn, P. Y., Mechanisms of Adsorbent Action in Beverage Stabilization. *Journal of Agricultural and Food Chemistry* **1997**, 45, (11), 4275-4280.
- (56) Domingues, R. C. C.; Faria Junior, S. B.; Silva, R. B.; Cardoso, V. L.; Reis, M. H. M., Clarification of passion fruit juice with chitosan: Effects of coagulation process variables and comparison with centrifugation and enzymatic treatments. *Process Biochemistry* **2012**, 47, (3), 467-471.
- (57) Chatterjee, S.; Chatterjee, S.; Chatterjee, B. P.; Guha, A. K., Clarification of fruit juice with chitosan. *Process Biochemistry* **2004**, 39, (12), 2229-2232.

- (58) Martín-Diana, A. B.; Rico, D.; Barat, J. M.; Barry-Ryan, C., Orange juices enriched with chitosan: Optimisation for extending the shelf-life. *Innovative Food Science & Emerging Technologies* **2009**, 10, (4), 590-600.
- (59) Al-Farsi, M. A., Clarification of date juice. *International Journal of Food Science & Technology* **2003**, 38, (3), 241-245.
- (60) Nasehi, S. M.; Ansari, S.; Sarshar, M., Removal of dark colored compounds from date syrup using activated carbon: A kinetic study. *Journal of Food Engineering* **2012**, 111, (3), 490-495.
- (61) Fabio Alessio Romano Dionisi, R. J. C. Sugar cane juice clarification process. U.S. Patent US 20090126720 A1, May 21, 2009.
- (62) Thai, C. C. D.; Bakir, H.; Doherty, W. O. S., Insights to the Clarification of Sugar Cane Juice Expressed from Sugar Cane Stalk and Trash. *Journal of Agricultural and Food Chemistry* **2012**, 60, (11), 2916-2923.
- (63) Laksameethanasana, P.; Somla, N.; Janprem, S.; Phochuen, N., Clarification of sugarcane juice for syrup production. *Procedia Engineering* **2012**, 32, (0), 141-147.
- (64) Pieter Willem van der Poel, H. M. S., Thomas K. Schwartz, *Sugar Technology: Beet and Cane Sugar Manufacture In illustrated ed.*; Verlag Dr Albert Bartens KG: Berlin: Bartens, 1998; p 1118.
- (65) Chen, Y.-C.; Jaczynski, J., Protein Recovery from Rainbow Trout (*Oncorhynchus mykiss*) Processing Byproducts via Isoelectric Solubilization/Precipitation and Its Gelation Properties As Affected by Functional Additives. *Journal of Agricultural and Food Chemistry* **2007**, 55, (22), 9079-9088.
- (66) Taskaya, L.; Jaczynski, J., Flocculation-enhanced protein recovery from fish processing by-products by isoelectric solubilization/precipitation. *LWT - Food Science and Technology* **2009**, 42, (2), 570-575.
- (67) Dawson, P. L.; Sheldon, B. W.; Ball, H. R., Extraction of Lipid and Pigment Components from Mechanically Deboned Chicken Meat. *Journal of Food Science* **1988**, 53, (6), 1615-1617.
- (68) Taherghorabi, R.; Beamer, S. K.; Matak, K. E.; Jaczynski, J., Effect of isoelectric solubilization/precipitation and titanium dioxide on whitening and texture of proteins recovered from dark chicken-meat processing by-products. *LWT - Food Science and Technology* **2011**, 44, (4), 896-903.
- (69) Smyth, A. B.; O'Neill, E., Heat-Induced Gelation Properties of Surimi From Mechanically Separated Chicken. *Journal of Food Science* **1997**, 62, (2), 326-330.
- (70) Halverson, F. Process for the flocculation of suspended solids. U.S. Patent US 4342653 A, Aug 3, 1982.
- (71) Lawrence J. Connelly, P. F. R., Dodd W. Fong, Ralph W. Kaesler Sulphonate-containing terpolymers as flocculants for suspended solids. Grant Patent CA 1285450 C, Jul 2, 1991.
- (72) Nuntiya, N. C. a. A., Influence of pH, Electrolytes and Polymers on Flocculation of Kaolin Particle. *Chiang Mai J. Sci.* **2008**, 35, (1), 11-16.
- (73) Raluca Nicu, E. B., Ruben Miranda, Angeles Blanco, Flocculation Efficiency of Chitosan for Papermaking Applications. *BioResources* **2013**, 8, (1), 768-784.
- (74) Zakrajšek, N.; Fuente, E.; Blanco, A.; Golob, J., Influence of Cationic Starch Adsorption on Fiber Flocculation. *Chemical Engineering & Technology* **2009**, 32, (8), 1259-1265.
- (75) Lauri Kuutti, S. H., Sari Hyvarinen, Hannu Mikkonen, Riikka Koski, Soili Peltonen, Tapani Suortti, Hanna Kyllönen, PROPERTIES AND FLOCCULATION EFFICIENCY OF CATIONIZED BIOPOLYMERS AND THEIR APPLICABILITY IN PAPERMAKING AND IN CONDITIONING OF PULP AND PAPER SLUDGE. *BioResources* **2011**, 6, (3), 2836-2850.
- (76) Jaroslav Melzer, H.-U. S. Retention aids and flocculants based on polyacrylamides. Grant Patent CA 1050680 A1, Mar 13, 1979.
- (77) Bratskaya, S.; Schwarz, S.; Liebert, T.; Heinze, T., Starch derivatives of high degree of functionalization: 10. Flocculation of kaolin dispersions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2005**, 254, (1-3), 75-80.
- (78) Singhabhandhu, A.; Tezuka, T., A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock. *Energy* **2010**, 35, (6), 2493-2504.



- (79) Sdrula, N., A study using classical or membrane separation in the biodiesel process. *Desalination* **2010**, 250, (3), 1070-1072.
- (80) Wu, T. Y.; Mohammad, A. W.; Md. Jahim, J.; Anuar, N., Palm oil mill effluent (POME) treatment and bioresources recovery using ultrafiltration membrane: Effect of pressure on membrane fouling. *Biochemical Engineering Journal* **2007**, 35, (3), 309-317.
- (81) Aldo, B. T. O. J. C. G. P. R. Process for purifying crude glycerol. European Patent EP 0 358 255 A1, Mar 14, 1990.
- (82) Mah, S.-K.; Leo, C. P.; Wu, T. Y.; Chai, S.-P., A feasibility investigation on ultrafiltration of palm oil and oleic acid removal from glycerin solutions: Flux decline, fouling pattern, rejection and membrane characterizations. *Journal of Membrane Science* **2012**, 389, (0), 245-256.
- (83) Wagner Celio Ferraz Lourenco, R. M., Jose Eduardo Cielo Process for the purification of crude glycerol. European Patent EP 2295394 A1, Mar 16, 2011.
- (84) Singh, V.; Kumar, P.; Sanghi, R., Use of microwave irradiation in the grafting modification of the polysaccharides – A review. *Progress in Polymer Science* **2012**, 37, (2), 340-364.
- (85) RAVI KUMAR, A. S., N. MAHADEVAN, Grafting Modification of the Polysaccharide by the use of Microwave irradiation – A review. *International Journal of Recent Advances in Pharmaceutical Research* **2012**, 2, (2), 45-53.
- (86) Buléon, A.; Colonna, P.; Planchot, V.; Ball, S., Starch granules: structure and biosynthesis. *International Journal of Biological Macromolecules* **1998**, 23, (2), 85-112.
- (87) Singh, R.; Nayak, B.; Biswal, D.; Tripathy, T.; Banik, K., Biobased polymeric flocculants for industrial effluent treatment. *Materials Research Innovations* **2003**, 7, (5), 331-340.
- (88) Mishra, A.; Yadav, A.; Agarwal, M.; Rajani, S., Polyacrylonitrile-grafted Plantago psyllium mucilage for the removal of suspended and dissolved solids from tannery effluent. *Colloid and Polymer Science* **2004**, 282, (3), 300-303.
- (89) Adhikary, P.; Tiwari, K. N.; Singh, R. P., Synthesis, characterization, and flocculation characteristics of polyacrylamide-grafted glycogen. *Journal of Applied Polymer Science* **2007**, 103, (2), 773-778.
- (90) Mishra, S.; Mukul, A.; Sen, G.; Jha, U., Microwave assisted synthesis of polyacrylamide grafted starch (St-g-PAM) and its applicability as flocculant for water treatment. *International Journal of Biological Macromolecules* **2011**, 48, (1), 106-111.
- (91) Pal, S.; Ghorai, S.; Dash, M. K.; Ghosh, S.; Udayabhanu, G., Flocculation properties of polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) synthesised by conventional and microwave assisted method. *Journal of Hazardous Materials* **2011**, 192, (3), 1580-1588.
- (92) Ghosh, S.; Jha, U.; Pal, S., High performance polymeric flocculant based on hydrolyzed polyacrylamide grafted tamarind kernel polysaccharide (Hyd. TKP-g-PAM). *Bioresource Technology* **2011**, 102, (2), 2137-2139.
- (93) Sen, G.; Mishra, S.; Rani, G. U.; Rani, P.; Prasad, R., Microwave initiated synthesis of polyacrylamide grafted Psyllium and its application as a flocculant. *International Journal of Biological Macromolecules* **2012**, 50, (2), 369-375.
- (94) Agarwal, M.; Srinivasan, R.; Mishra, A., Synthesis of Plantago Psyllium Mucilage Grafted Polyacrylamide and its Flocculation Efficiency in Tannery and Domestic Wastewater. *Journal of Polymer Research* **2002**, 9, (1), 69-73.
- (95) Mishra, A.; Srinivasan, R.; Bajpai, M.; Dubey, R., Use of polyacrylamide-grafted Plantago psyllium mucilage as a flocculant for treatment of textile wastewater. *Colloid and Polymer Science* **2004**, 282, (7), 722-727.
- (96) Rajani Srinivasan, M. A. a. A. M., Plantago psyllium-grafted-polyacrylonitrile--Synthesis, characterization and its use in suspended and dissolved solid removal from textile effluent. *Water Quality Research Journal of Canada* **2002**, 37, (2), 371-378.
- (97) Kumar, R.; Sharma, K.; Tiwary, K. P.; Sen, G., Polymethacrylic acid grafted psyllium (Psy-g-PMA): a novel material for waste water treatment. *Applied Water Science* **2013**, 3, (1), 285-291.

- (98) Mishra, S.; Sinha, S.; Dey, K. P.; Sen, G., Synthesis, characterization and applications of polymethylmethacrylate grafted psyllium as flocculant. *Carbohydrate Polymers* **2014**, 99, (0), 462-468.
- (99) Ghosh, S.; Sen, G.; Jha, U.; Pal, S., Novel biodegradable polymeric flocculant based on polyacrylamide-grafted tamarind kernel polysaccharide. *Bioresource Technology* **2010**, 101, (24), 9638-9644.
- (100) Pal, S.; Sen, G.; Ghosh, S.; Singh, R. P., High performance polymeric flocculants based on modified polysaccharides—Microwave assisted synthesis. *Carbohydrate Polymers* **2012**, 87, (1), 336-342.
- (101) Odian, G., Principles of Polymerization. In Fourth ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, March 2004; p 789.
- (102) Kalia, S.; Sabaa, M.; Kango, S., Polymer Grafting: A Versatile Means to Modify the Polysaccharides. In *Polysaccharide Based Graft Copolymers*, Kalia, S.; Sabaa, M. W., Eds. Springer Berlin Heidelberg: 2013; pp 1-14.
- (103) Subramanian, U.; Ahmed, A. E., Intestinal Toxicity of Acrylonitrile: In Vitro Metabolism by Intestinal Cytochrome P450 2E1. *Toxicology and Applied Pharmacology* **1995**, 135, (1), 1-8.
- (104) Mishra, S.; Sen, G.; Rani, G. U.; Sinha, S., Microwave assisted synthesis of polyacrylamide grafted agar (Ag-g-PAM) and its application as flocculant for wastewater treatment. *International Journal of Biological Macromolecules* **2011**, 49, (4), 591-598.
- (105) Sen, G.; Kumar, R.; Ghosh, S.; Pal, S., A novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch. *Carbohydrate Polymers* **2009**, 77, (4), 822-831.
- (106) Brostow, W.; Pal, S.; Singh, R. P., A model of flocculation. *Materials Letters* **2007**, 61, (22), 4381-4384.
- (107) Tripathy, T.; Singh, R. P., High performance flocculating agent based on partially hydrolysed sodium alginate-g-polyacrylamide. *European Polymer Journal* **2000**, 36, (7), 1471-1476.
- (108) Ram P. Singh, S. P., S. Krishnamoorthy, P. Adhikary and Sk. Akbar Ali, High-technology materials based on modified polysaccharides. *Pure and Applied Chemistry* **2009**, 81, (3), 525-547.
- (109) Das, R.; Ghorai, S.; Pal, S., Flocculation characteristics of polyacrylamide grafted hydroxypropyl methyl cellulose: An efficient biodegradable flocculant. *Chemical Engineering Journal* **2013**, 229, (0), 144-152.
- (110) Yang, Z.; Yang, H.; Jiang, Z.; Cai, T.; Li, H.; Li, H.; Li, A.; Cheng, R., Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethyl chitosan-graft-polyacrylamide. *Journal of Hazardous Materials* **2013**, 254-255, (0), 36-45.
- (111) A. Shipp, G. L., R. Gentry, T. McDonald, H. Bartow, J. Bounds, N. Macdonald, H. Clewell, B. Allen and C. Van Landingham, Acrylamide: Review of Toxicity Data and Dose-Response Analyses for Cancer and Noncancer Effects. *Critical Reviews in Toxicology* **2006**, 36, (6-7), 481-608.