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Review

A review on application of flocculants in wastewater treatment

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ABSTRACT

Flocculation is an essential phenomenon in industrial wastewater treatment. Inorganic coagulants (salts of multivalent metals) are being commonly used due to its low cost and ease of use. However, their application is constrained with low flocculating efficiency and the presence of residue metal concentration in the treated water. Organic polymeric flocculants are widely used nowadays due to its remarkable ability to flocculate efficiently with low dosage. However, its application is associated with lack of biodegradability and dispersion of monomers residue in water that may represent a health hazard. Therefore, biopolymers based flocculants have been attracting wide interest of researchers because they have the advantages of biodegradability and environmental friendly. But, natural flocculants are needed in large dosage due to its moderate flocculating efficiency and shorter shelf life. Thus, in order to combine the best properties of both, synthetic polymers are grafted onto the backbone of natural polymers to obtain tailor-made grafted flocculants. This paper gives an overview of the development of different types of flocculants that were being investigated for treatment of industrial wastewater. Furthermore, their flocculation performance will be reviewed and the flocculation mechanism will be discussed.

Keywords: Coagulation–flocculation; Direct flocculation; Bio-flocculants; Grafted flocculants; Flocculation mechanism; Wastewater treatment

Contents

Abbreviations: BOD_5, 5 days biochemical oxygen demand; CD, charge density; C-F, coagulation–flocculation; COD, chemical oxygen demand; C-PAM, cationic polyacrylamide; D-F, direct flocculation; LDS, light diffraction scattering; MW, molecular weight; RP, reactive phosphorus; SVI, sludge volume index; TDS, total dissolved solids; $TOC_{soluble}$, soluble total organic carbon; TP, total phosphorus; TS, total solids; TSS, total suspended solids.

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1. Introduction

The wastewater produced from different kinds of industries normally contains very fine suspended solids, dissolved solids, inorganic and organic particles, metals and other impurities. Due to very small size of the particles and presence of surface charge, the task to bring these particles closer to make heavier mass for settling and filtration becomes challenging (Bratby, 2006). Hence, removal of these colloidal particles from the wastewater becomes a serious challenge for the industries (Divakaran and Sivasankara Pillai, 2001; Nasser and James, 2006). Various traditional and advanced technologies have been utilised to remove the colloidal particles from wastewater; such as ion exchange, membrane filtration, precipitation, flotation, solvent extraction, adsorption, coagulation, flocculation, biological and electrolytic methods (Radoiu et al., 2004).

Among those methods, coagulation/flocculation is one of the most widely used solid–liquid separation process for the removal of suspended and dissolved solids, colloids and organic matter present in industrial wastewater (Renault et al., 2009b). It is a simple and efficient method for wastewater treatment, and has been extensively used for the treatment of various types of wastewater such as palm oil mill effluent, textile wastewater, pulp mill wastewater, oily wastewater, sanitary landfill leachates and others (Ahmad et al., 2005; Tatsi et al., 2003; Wong et al., 2006; Yue et al., 2008; Zhong et al., 2003). In this process, after the addition of coagulant and/or flocculant, finely divided or dispersed particles are aggregated or agglomerated together to form large particles of such a size (flocs) which settle and cause clarification of the system (Sharma et al., 2006).

Coagulation is mainly induced by inorganic metal salts, such as aluminium sulphate and ferric chloride. In some cases, these metal salts can be used in wastewater treatment without assistance of flocculant(s) (Wang et al., 2011; Zhong et al., 2003). Nowadays, the usage of inorganic coagulants has been reduced due to its inefficiency in wastewater treatment with small dosage and narrow application. In most of the cases, polymeric flocculants are preferable to facilitate separation process either with or without coagulant. Up to now, a wide range of flocculants (also known as coagulant aids) have been developed or designed to improve the flocculation process in wastewater treatment including synthetic or natural organic flocculants and grafted flocculants.

Polymeric flocculants, synthetic as well as natural have become very popular in industrial effluent treatment due to their natural inertness to pH changes, high efficiency with low dosage, and easy handling (Singh et al., 2000). However, the synthetic polymeric flocculants have the main problems of non-biodegradability and unfriendly to the environment, while the natural flocculants are concerned with moderate efficiency and short shelf life. In order to combine the best properties of synthetic and natural polymers, grafted flocculants have been synthesised and studied extensively recently.

As flocculants plays the major role in flocculation process, the search for high efficient and cost-effective flocculants has always become the challenge in many studies. The main process variables that are commonly measured to justify the flocculation efficiency include settling rate of flocs, sediment volume (sludge volume index, SVI), percent solids settled, turbidity or supernatant clarity, percentage of pollutants removal or water recovery depending on the industrial application (Bohuslav Dobias, 2005). All these output variables are actually manifestations of the floc or aggregate size distribution and the shape and structure of flocs produced during the flocculation process. Bigger, stronger and denser flocs are preferable for good sedimentation, easy filtration and high clarification.

The present review article classifies the flocculants that have been studied and applied in wastewater treatment into three categories including chemical coagulants/flocculants, natural bio-flocculants and grafted flocculants as shown in Fig. 1. Chemical coagulants/flocculants are conventionally applied in wastewater treatment and derived from chemically/petroleum-based materials. Natural bio-flocculants are extensively explored on the past few years and sourced from natural materials. Meanwhile, grafted flocculants are investigated recently and synthesised by combining the properties of chemical and natural flocculants. This review has compiled all the recent literature about flocculants and is expected to provide an overview of recent information regarding the development and application of various flocculants in treating wastewater. In addition, its flocculating efficiency

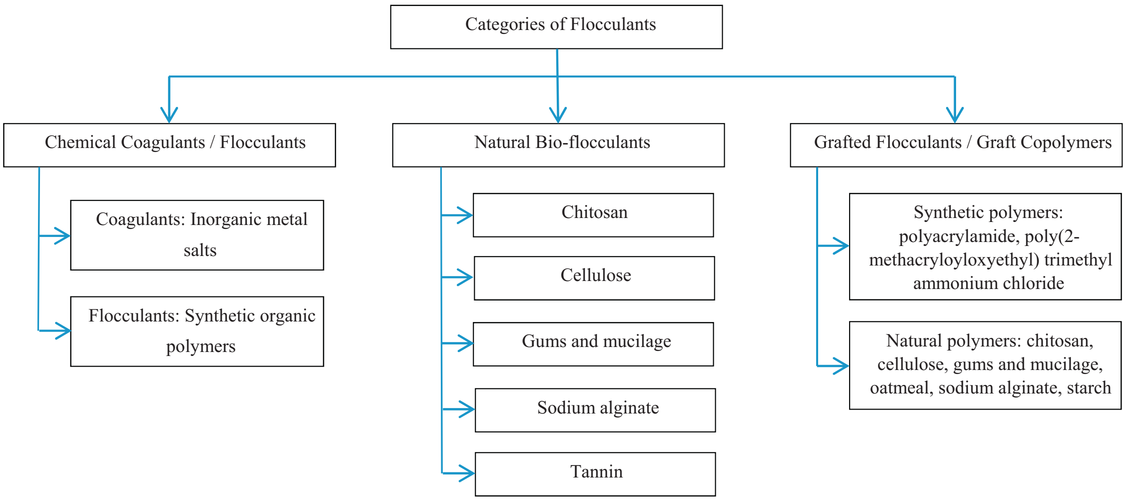

Fig. 1 – Classification of flocculants.

and the relevant flocculating mechanisms for treatment of wastewater are presented and discussed. It is an essential area to be reviewed here considering there is no systematic compilation available up to date and this information is expected to be significant for future development and scaling purposes.

2. Coagulation–flocculation and direct flocculation

There are two methods of wastewater treatment which are coagulation–flocculation and direct flocculation. The summary of their application in different types of wastewater is presented in Tables 1 and 2.

2.1. *Coagulation–flocculation*

Coagulation–flocculation is the conventional treatment method where the cationic inorganic metal salts are commonly used as coagulants and long chains non-ionic or anionic polymers are usually employed as flocculants (Chong, 2012). It is generally known that most of the suspended particles in wastewater carry negative charge in aqueous medium. After addition of inorganic coagulant, metal salts will hydrolyse rapidly in wastewater at isoelectric point to form cationic species, which are adsorbed by negatively charged colloidal particles, resulting in simultaneous surface charge reduction and formation of micro-flocs (Suopajärvi et al., 2013). However, the coagulation process is not always perfect as it may result in small flocs when coagulation takes place at low temperature or produce fragile flocs which break up when subjected to physical forces. It is not only essential to conquer these problems but also to improve the process to obtain good quality effluent and rapid sedimentation of the flocs formed.

To do so, anionic/non-ionic polymeric flocculants are widely used to bring together and agglomerate the slow-settling micro-flocs formed by the coagulant to form larger and denser flocs, thereby facilitating their removal in subsequent sedimentation, flotation and filtration stages (Lee et al., 2012). The use of flocculants not only can increase the density and the solidity of the flocs formed, it also can reduce the consumption of coagulants and increases the reliability of the work and the throughput capacity of the treatment plant (Radoiu et al., 2004). A study has reported that the combined use of coagulant (ferric chloride) and polyelectrolyte (non-ionic polyacrylamide) resulted in the production of sludge volume with reduction of 60% of the amount produced when coagulant was solely used for the treatment of beverage industrial wastewater (Amuda and Amoo, 2007).

As shown in Table 1, many studies have proved that the addition of a polymeric flocculant to an inorganic coagulant showed better removal where it was effective in the reduction of environmental concerned parameters (>90% generally) such as chemical oxygen demand (COD), total suspended solids (TSS), turbidity and colour, reduce the amount of coagulant used and thus reduced the cost of the coagulation/flocculation process (Ahmad et al., 2005, 2008; Amuda and Alade, 2006; Irfan et al., 2013; Martín et al., 2011; Sher et al., 2013; Yang et al., 2010; Zayas Péerez et al., 2007).

2.2. *Direct flocculation*

In order to save the treatment cost and time, direct flocculation was proposed and investigated in some studies. In direct flocculation, medium charge density with high molecular weight cationic polymers is normally used. It has dual functions: (1) neutralise the negative charges of the colloidal particles and (2) bridge the aggregated destabilised particles together to form flocs (Chong, 2012). In those research works, addition of coagulant and pH adjustment was not needed, only cationic and/or anionic polymers were used in clarification of wastewater. As presented in Table 2, the polymers used for direct flocculation are workable in all range of pH values including acidic, neutral and base medium. The use of high molecular weight polymers could bridge the colloidal particles with loops and tails at any pH condition. This phenomenon is in contrast with the coagulation–flocculation process where the complex precipitates of metal hydroxides are only obtained at the desired pH after addition of coagulant and pH alteration.

In addition, direct flocculation generates less volume of sludge because the flocs formed with strong bridging mechanism are densed and closely packed. In addition, as the polymers are organic in nature, thus some of the sludge generated is readily for disposal after simple treatment. This advantage will lead to reduction of overall treatment cost. A case study has been conducted to evaluate the differences between coagulation–flocculation and direct flocculation process in treatment of palm oil mill effluent (POME) (Chong, 2012). The preliminary cost analysis conducted by

Table 1 – Application of coagulation–flocculation process with chemical coagulant(s) and flocculant(s) in wastewater treatment.

Coagulant(s)	Flocculant(s)	Type of wastewater	Optimum results		Reference
Ferric chloride, aluminium sulphate and lime	Neutral (N200), two cationic (K1370 and K506) and an anionic (A321) polyelectrolytes	Sanitary landfill leachates	COD Colour	About 80% removal About 100% removal	Tatsi et al. (2003)
Sodium diethyldithiocarbamate (DDTC) – trapping agent	Anionic polyacrylamide	Copper electroplating wastewater	Copper	99.6% removal	Li et al. (2003)
Modified alum (Envifloc-40L)	Industrial grade flocculant (Profloc 4190)	Palm oil mill effluent	Turbidity Water recovery	>98% removal 78%	Ahmad et al. (2005)
Lime, ferrous sulphate	Four cationic (FO-4700-SH, FO-4490-SH, FO-4350-SHU and FO-4190-SH) and two anionic (AN 934-SH and FLOCAN 23) polyelectrolytes	Olive mill effluent	TSS TP COD	30–95% removal 30–80% removal 10–40% removal	Ginos et al. (2006)
Alum, ferric chloride and ferric sulfate	Anionic polyacrylamide	Abattoir wastewater	COD TSS TP	94% removal 94% removal 97% removal	Amuda and Alade (2006)
Commercial coagulant: T-1	Commercial flocculants: Ecofloc 6260, Ecofloc 6700, Ecofloc 6705, Ecofloc 5400, Ecofloc 6708	Coffee wastewater	COD	55–60% removal	Zayas Péerez et al. (2007)
Ferric chloride	Non-ionic polyacrylamide	Beverage industrial wastewater	COD TP TSS	91% removal 99% removal 97% removal	Amuda and Amoo (2007)
Alum/ferric salt	Synthetic cyanoguanidine-formaldehyde based polymer	Synthetic reactive dyes wastewater	Colour	Almost 100% removal	Joo et al. (2007)
		Real reactive dye wastewater	Colour	62% removal	
Alum and polyaluminium chloride (PACl)	Cationic (Organopol 5415) and anionic (Chemfloc 430A) polyacrylamides	Pulp and paper mill wastewater	Turbidity TSS COD SVI Settling time	99.7% removal 99.5% removal 95.6% removal 38 ml/g 12 s	Ahmad et al. (2008)
Palm oil mill boiler (POMB) – adsorbent	Cationic polymer (KP 1200B) and anionic polymer (AP 120C)	Ceramic industry wastewater	Boron TSS	15–3 mg/L 2000–5 mg/L	Chong et al. (2009)
Mixture of ferric chloride and polyaluminium chloride	Cationic, anionic and non-ionic polyacrylamides	High-phosphorus hematite flotation wastewater	Turbidity	13,530–12NTU	Yang et al. (2010)
Aluminium polychloride	Anionic polyacrylamide (Actipol A-401)	Wastewater from sauce manufacturing plant	COD	82% removal	Martín et al. (2011)

			Turbidity $TOC_{soluble}$	72% removal 13% removal	
Aluminium sulphate	Anionic polyacrylamide (Magnafloc 155)	Industrial polymer effluent	COD TSS Turbidity	98% removal 91% removal 99% removal	Sher et al. (2013)
Alum, ferric chloride, ferrous sulphate, aluminium chloride, poly-aluminium chloride	Cationic and anionic polyacrylamides	Pulp and paper mill wastewater	COD TSS Colour	76% removal 95% removal 95% removal	Irfan et al. (2013)

the author showed that the total treatment cost of conventional treatment was 3.6 times higher than direct flocculation due to larger volumes of phyto-toxic sludge produced from coagulation–flocculation process.

As presented in Table 2, direct flocculation was workable in treatment of oily wastewater (Zhong et al., 2003), olive mill effluent (Sarika et al., 2005), aquaculture wastewater (Ebeling et al., 2005), coal waste slurry (Sabah and Erkan, 2006), pulp and paper mill wastewater (Wong et al., 2006; Razali et al., 2011), and textile wastewater (Kang et al., 2007; Yue et al., 2008). The research findings showed that high flocculation efficiency could be achieved by using single polymer only as flocculant where more than 90% removal of turbidity, TSS, COD and colour could be observed in specific wastewater.

2.3. *Comparison between coagulation–flocculation and direct flocculation*

As presented above, direct flocculation has been applied to replace coagulation–flocculation in certain types of wastewater treatment. However, its application is mostly limited to organic-based wastewater with high concentration of suspended and colloidal solids; such as food, paper and pulp, and textile effluents. Thus, conventional coagulation–flocculation process is still preferable and widely employed by most of the industries because it can be applied for both inorganic and organic-based wastewater with suspended and dissolved solid constituents (Chong, 2012). As a summary, each treatment process has its own pros and cons and the type of wastewater is the main factor that influences the selection between coagulation–flocculation and direct flocculation. Regardless of limited application of direct flocculation, this process is still worthwhile to be explored due to its advantages of less chemical used in the treatment, simpler process, less sludge is produced and lower treatment cost. An overview of the differences between coagulation–flocculation and direct flocculation and the general procedures for each process are presented in Table 3 and Fig. 2, respectively.

3. Chemical coagulants and flocculants

The conventional chemicals that are widely applied in industrial wastewater treatment can be classified into two major groups: inorganic mineral additives/metal salts which are used as coagulants and organic polymeric materials that are employed as flocculants.

3.1. *Inorganic coagulants*

Inorganic salts of multivalent metals such as alum, polyaluminium chloride, ferric chloride, ferrous sulphate, calcium chloride and magnesium chloride have been widely used for decades as coagulant (Joo et al., 2007). It is mainly because of its advantage of low cost, where their market price is very much lower compared to the chemical flocculants as shown in Table 4.

However, the application of inorganic coagulants in wastewater is quite limited nowadays and has been reduced due to numerous disadvantages. As reported in many studies, its usage would cause two important environmental consequences which are the production of large volumes of metal hydroxide (toxic) sludge which will create disposal problem and an increase in metal (e.g. aluminium) concentration in the treated water which may have human health implications

Table 2 – Application of direct flocculation with chemical flocculant(s) in wastewater treatment.

Flocculant(s)	Type of wastewater and its pH value	Optimum results		Reference
Derivative of polyacrylamide (Poly1 and 3530S), polyacrylamide	Oily wastewater from refinery plant	Oil	6 g/L to 220 mg/L	Zhong et al. (2003)
		COD	3 g/L to 668 mg/L	
Four cationic (FO-4700-SH, FO-4490-SH, FO-4350-SHU and FO-4190-SH) and two anionic (FLOCAN 23 and AN 934-SH) polyelectrolytes	Olive mill effluent, 5.5–6.7	TSS	Nearly 100% removal	Sarika et al. (2005)
		COD	55% removal	
		BOD_5	23% removal	
Cationic polyamine (Magnafloc LT 7991), cationic organic polyelectrolytes (Magnafloc LT 7992 and 7995), cationic polyacrylamide (Hyperfloc CE 854 and CE 1950), copolymer of quaternary acrylate salt and acrylamide (Magnafloc 22S)	Aquaculture wastewater, 6.97–7.78	TSS	99% removal	Ebeling et al. (2005)
		RP	92–95% removal	
Cationic (FO-4700-SH and FO-4490-SH) polyelectrolytes	Olive mill effluent, 5.1–5.3	TSS	97–99% removal	Ginos et al. (2006)
		TP	50–56% removal	
		COD	17–35% removal	
Polyacrylamide-based polymers (anionic: Praestol 2515, Praestol 2540, non-ionic: Magnofloc 351, cationic: Praestol 857 BS)	Coal waste slurry, 8.3	Turbidity	25–6.8NTU	Sabah and Erkan (2006)
Cationic (Organopol 5415, Organopol 5020, Organopol 5470, Organopol 5450, Chemfloc 1515C) and anionic (Organopol 5540, Chemfloc 430A, AN 913, AN 913SH) polyacrylamides	Pulp and paper mill wastewater, 7.3–8.3	Turbidity	95% removal	Wong et al. (2006)
		TSS	98% removal	
		COD	93% removal	
		SVI	14 ml/g	
		Water recovery	91%	
Cationic polydiallyldimethylammonium chloride (PDADMAC)	Simulated reactive dye wastewater, 7	Colour	>90% removal	Kang et al. (2007)
Cationic polyamine	Simulated dye liquor wastewater, 6.63–7.89	Colour	96% removal	Yue et al. (2008)
	Actual printing and dyeing wastewater, 11.2	Colour	90% removal	
		COD	89% removal	
Cationic polydiallyldimethylammonium chloride (polyDADMAC)	Pulp and paper mill wastewater, 7	Turbidity	91% removal	Razali et al. (2011)
		TSS	Nearly 100% removal	
		COD	98% removal	

Table 3 – Comparison between coagulation–flocculation and direct flocculation.

Comparison criteria	Coagulation–flocculation	Direct flocculation
Application	Inorganic and organic-based wastewater	Organic-based wastewater
Treatment ability	Suspended and dissolved solid particles	Suspended and colloidal particles
Types of chemicals to be used	Coagulant(s) (e.g. inorganic metal salts) followed by polymeric flocculant(s) (usually anionic)	Cationic or anionic polymeric flocculants (usually cationic)
Treatment process	More complicated, requires the pH adjustment	Simpler, without pH adjustment
Sludge generated	More sludge is produced, may contain metals and monomers residue	Less sludge is produced, may contain monomers residue
Overall treatment cost	More expensive due to chemicals cost (coagulant and flocculant) and large sludge treatment cost	Less expensive because only one chemical is used and less sludge treatment cost
Flocculating mechanism	Charge neutralisation (coagulation) followed by bridging (flocculation)	Charge neutralisation and bridging occur concurrently

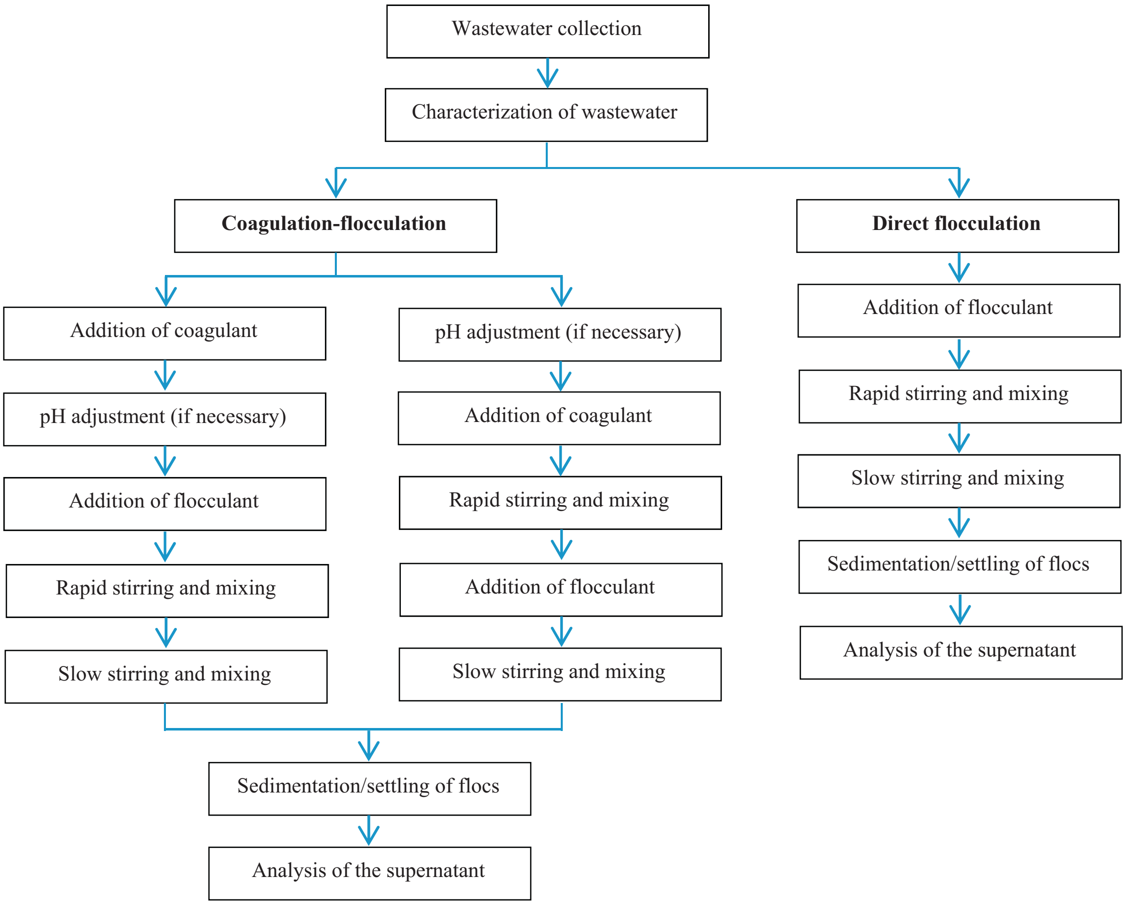

Fig. 2 – General procedures for coagulation–flocculation and direct flocculation process (Joo et al., 2007; Martín et al., 2011; Razali et al., 2011; Sher et al., 2013; Yue et al., 2008).

(Flaten, 2001; Ward et al., 2006). Recent epidemiological, neuropathological and biochemical studies suggest a possible link between the neurotoxicity of aluminium and the pathogenesis of Alzheimer's disease (Banks et al., 2006; Polizzi et al., 2002).

Other drawbacks include large amount is required for efficient flocculation, highly sensitive to pH, inefficient towards very fine particles, inefficient in cold water (e.g. polyaluminium chloride) and applicable only to a few disperse systems (Bratby, 2006; Sharma et al., 2006). In order to minimise the drawbacks of inorganic flocculants, many factors have been taken into consideration to find the alternative and reduce the dosage of the harmful inorganic flocculants.

3.2. *Organic synthetic flocculants*

In recent years, many synthetic polymers have been used as the main flocculants (coagulant aids) which could enhance the coagulation and flocculation efficiency with promising

Table 4 – Market prices for bulk sales of chemical coagulants and flocculants (Sarika et al., 2005).

Chemical materials	Coagulants		Cationic flocculants		Anionic flocculants	
	Lime	$FeCl_3$	FO-4700	FO-4490	FLOCAN	AN 934
Price, €/tonne	130	450	2980	2800	2500	2550

Table 5 – The main characteristics of synthetic polymeric flocculants.

Characteristics	Categorisation	
Nature of charges	Amphoteric/anionic/cationic/non-ionic	
Molecular weight	Low	1–3 millions
	Medium	3–6 millions
	Standard	6–10 millions
	High	10–15 millions
	Very high	Greater than 15 millions
Charge density	Low	1–10%
	Medium	10–40%
	High	40–80%
	Very high	80–100%

results have been reported (Ahmad et al., 2008; Kang et al., 2007). Commercial organic flocculants are mostly linear water soluble polymers which are based on repeating units of various monomers such as acrylamide and acrylic acid. In most cases, they are derived from oil-based and non-renewable raw materials (Suopajärvi et al., 2013). Commonly used polymeric flocculants include polyacrylamide, polyacrylic acid, poly(diallyl dimethyl ammonium chloride) (DADMAC), polyamine and others (Singh et al., 2000).

Polymers can vary in molecular weight, structure (linear versus branched), amount of charge, charge type and composition but generally, the synthetic polymers are classified into four forms: cationic (positively charged), anionic (negatively charged), amphoteric (contains both cationic and anionic groups) and non-ionic (close to neutral). Strictly, ionic polymers are addressed as polyelectrolytes. The nature of the charges is the main parameter that will have significant effect on the efficiency of flocculation process followed by molecular weight and charge density (Table 5).

The use of organic polyelectrolytes in drinking water treatment was recently reviewed with emphasis on the types of polymers commonly available and the nature of the impurities to be removed (Bolto and Gregory, 2007). However, review of application of synthetic polymeric flocculants especially in wastewater treatment has not been reported before. Thus, the publications related to this area of study from year 2003 to 2013 are compiled and presented in Tables 1 and 2. It is obvious that the role of polymeric flocculants in wastewater treatment is very well established, where it has successfully removed colloidal particles and contaminants (pollutants) from various types of wastewater. The effectiveness of the flocculation was normally measured based on the reduction of turbidity, TSS, COD and colour, and most of the studies reported that more than 90% removal could be achieved at optimum conditions. By referring to the compilation data, it was noticed that polyacrylamide received great extent of utility in the industries due to its economical advantage and easy tailorability (Singh et al., 2000). It is possible to synthesise polyacrylamide with various functions (positive, negative or neutral charge) with various molecular weight and charge density where it can be used to produce a good settling performance at relatively low cost (Ahmad et al., 2008; Sharma et al., 2006).

The extensive use of polymers as flocculant is due to their distinct characteristic attributes. The polymers are convenient to use, immediately soluble in aqueous systems, and do not affect the pH of the medium. They are highly efficient with little quantities (e.g. few milligrams per litre) and the flocs formed during flocculation are bigger and stronger. Normally, an appropriate polyelectrolyte can increase floc size, and thus form strong and dense floc of regular shape which has good settling characteristics (Razali et al., 2011). The use of polymers in this way results in a substantial reduction of coagulant dose required with a 40–60% reduction is expected. The volume of sludge, the ionic load of the waste water (especially the level of aluminium), and the overall costs can be reduced (Bolto and Gregory, 2007).

Although water soluble synthetic polymers find wide applications as flocculants, however its market cost (Table 4) is at least ten times higher compared to chemical coagulants which influences its development. In addition, their usage is debatable because its application may cause environmental consequences and health hazards. Contaminants of synthetic polymers used in water and wastewater treatment generally arise from residual unreacted monomers (such as acrylamide, ethyleneimine), unreacted chemicals used to produce the monomer units (such as epichlorohydrin, formaldehyde and dimethylamine) and reaction by-products of the polymers in water (Criddle, 1990; Wu et al., 2012). Acrylamide is extremely toxic causing severe neurotoxic effects. Bolto and Gregory (2007) reported that the normally used anionic and non-ionic polymers are generally of low toxicity, but cationic polyelectrolytes are more toxic, especially to aquatic organisms.

Also, the majority of commercial polymers are also derived from petroleum-based raw materials using processing chemistry that is not always safe or environmentally friendly. Moreover, most synthetic polymer structures are resistant to biodegradation, which is usually extremely slow (Bolto and Gregory, 2007; Brostow et al., 2009) and their degraded products are considered hazardous because of the release of monomers that could enter in the food chain and may cause carcinogenic effect (Sharma et al., 2006; Singh et al., 2000). For these reasons, there is an increasing demand for environment-friendly and effective coagulant aids. In this respect, scientists around the world are trying to develop biopolymer based flocculants from natural sources that have the potential to substitute the synthetic flocculants.

4. Natural bio-flocculants

In recent years, as the demand on the environmentally friendly materials in treating water and wastewater continue to increase; bio-flocculants have emerged to be promising alternative materials to replace conventional flocculants. Natural organic flocculants which are based on polysaccharides or natural polymers may be of great interest because they are natural products and environmentally friendly behaviour. Compared with conventional chemical flocculants, bio-flocculants are safe and biodegradable polymers, fairly shear stable, easily available from reproducible agricultural resources and produce no secondary pollution (Bolto and Gregory, 2007). In addition, as biopolymers are biodegradable, the sludge can be efficiently degraded by microorganisms (Renault et al., 2009a). Thus, they have high potential to be applied not only in food and fermentation processes, pharmaceutical, cosmetic, downstream processing but also in water and wastewater treatment.

Bio-flocculants can destabilise the colloidal particles by increasing the ionic strength and giving some reduction in the zeta potential and thus a decreased thickness of the diffuse part of the electrical double layer. Or, they could specifically adsorb counterions to neutralise the particle charge because

Table 6 – Application of natural bio-flocculants in wastewater treatment.

Category	Coagulant(s)	Flocculant(s)	Type of wastewater	Optimum results		Reference
Chitosan	Iron(III) chloride	Chitosan	Pulp and paper mill wastewater	Turbidity	10–1.1NTU	Rodrigues et al. (2008)
				COD	1303–516 mg/L	
	–	Chitosan	Cardboard industry wastewater	COD	80% removal	Renault et al. (2009a,b)
				Turbidity	85% removal	
	–	Chitosan	Dye-containing solutions	Dye	99% removal	Szyguła et al. (2009)
Tannin	Aluminium sulphate	Anionic tannin	Drinking water	Turbidity	300–2FTU	Özacar and Şengil (2003)
	Chitosan	Anionic tannin	Ink-containing effluent from cardboard box-making factory	Colour	>99% removal	Roussy et al. (2005)
				COD	84% removal	
	–	Modified tannin (cationic Tanfloc)	Polluted surface water	Cu^{2+}, Zn^{2+} and Ni^{2+}	90%, 75% and 70% removal	Beltrán Heredia and Sánchez Martín (2009)
	–	Modified tannin (cationic Tanfloc)	Municipal wastewater	Turbidity	Almost 100% removal	Beltrán-Heredia and Sánchez-Martín (2009)
				COD	Around 50% removal	
				BOD_5	Around 50% removal	
Gums and mucilage	–	Anionic Psyllium mucilage (*Plantago psyllium*)	Sewage effluent	TSS	95% removal	Mishra et al. (2002)
			Tannery effluent	TSS	87% removal	
	–	Neutral Fenugreek mucilage (*Trigonella foenum-graecum*)	Tannery effluent	TSS	85% removal	Mishra et al. (2004)
				TDS	40% removal	
	–	Tamarind mucilage (*Tamarindus indica*)	Golden yellow dye and direct fast scarlet dye	Dye	60% and 25% removal	Mishra and Bajpai (2006)
	–	Mallow mucilage (*Malva sylvestris*)	Biologically treated effluent	Turbidity	67% removal	Anastasakis et al. (2009)
		Anionic Okra gum (*Hibiscus/Abelmoschus esculentus*)			74% removal	
	–	Anionic Isabgol mucilage (*Plantago ovata*)	Semi-aerobic landfill leachate	COD	64% removal	Al-Hamadani et al. (2011)
				Colour	90% removal	
				TSS	96% removal	
Sodium alginate	Aluminium sulphate	Anionic sodium alginate	Synthetic dye wastewater	Colour	93% removal	Wu et al. (2012)
			Actual textile wastewater	Colour	93.4% removal	
				COD	80.1% removal	
Cellulose	Aluminium sulphate	Anionic sodium carboxymethylcellulose (CMCNa)	Drinking water	Turbidity	93% removal	Khiari et al. (2010)
	Ferric sulphate	Anionic dicarboxylic acid nanocellulose (DCC)	Municipal wastewater	Turbidity	40–80% removal	Suopajärvi et al. (2013)
				COD	40–60% removal	

they have particular macromolecular structures with a variety of functional groups (e.g. carboxyl and hydroxyl groups) which can interact with contaminants (Özacar and Şengil, 2003). For many years, biopolymers based flocculants such as chitosan, tannins, cellulose, alginate, gums and mucilage have been attracting wide interest of researchers. The research work concerning the application of these bio-flocculants in wastewater treatment has been compiled and presented in Table 6.

4.1. *Chitosan*

Since most natural colloids are negatively charged, cationic polymers or polyelectrolytes are of particular interest as potential flocculants. Chitosan is one of the most promising biopolymer for extensive application due to its cationic behaviour. Chitosan is a partially deacetylated polymer obtained from the alkaline deacetylation of chitin, a biopolymer extracted from shellfish sources. It is a linear hydrophilic amino-polysaccharide with a rigid structure containing both glucosamine and acetylglucosamine units. It is insoluble in either water or organic solvents but soluble in dilute organic acids such as acetic acid and formic acid and inorganic acids (with the remarkable exception of sulphuric acid) where the free amino groups are protonated and the biopolymer becomes fully soluble (Renault et al., 2009a; Szyguła et al., 2009). At acidic pH (below ~pH 5), chitosan becomes a soluble cationic polymer with high charge density (Rinaudo, 2006). Thus, treatment of wastewater with chitosan dissolved in acids produces protonated amine groups along the chain and this facilitates electrostatic interactions between polymer chains and the negatively charged contaminants (metal anions, dyes, organic compounds, etc.) (Renault et al., 2009a).

This amino-biopolymer possesses several intrinsic characteristics such as high cationic charge density (due to the presence of primary amino groups) (Guibal and Roussy, 2007) and long polymer chains with high molecular weight, thus make it an effective coagulant and/or flocculant for the removal of contaminants in the suspended and dissolved state (Guibal et al., 2006; No and Meyers, 2000; Renault et al., 2009a). As the active amino groups ($-NH_2$) in the chitosan molecule can be protonated with H^+ in water into a cationic polyelectrolyte (Jaafari et al., 2004) the molecule has characteristics of static attraction and adsorption. Besides, chitosan can also flocculate particles into bigger flocs which become deposited. Therefore, the development of chitosan-based materials as useful coagulants and flocculants is an expanding field in the area of water and wastewater treatment due to its high affinity for many classes of contaminants. Numerous works have demonstrated its outstanding coagulation and flocculation properties for dye molecules in dye-containing solutions (Guibal and Roussy, 2007) or textile wastewater (Szyguła et al., 2009), organic matter (e.g. lignin and chlorinated compounds) in pulp and paper mill wastewater (Rodrigues et al., 2008), heavy metals and phenolic compounds in cardboard-mill wastewater (Renault et al., 2009b), and inorganic suspensions in kaolinite suspension (Li et al., 2013).

4.2. *Tannin*

Tannin is a biodegradable anionic polymer (Özacar and Şengil, 2000) which comes from vegetal secondary metabolytes such as bark, fruits, leaves and others (Beltrán Heredia and Sánchez Martín, 2009). Its flocculating property has been tested in removal of suspended and colloidal materials in drinking water treatment (Özacar and Şengil, 2003), removal of suspended matters from synthetic raw water (Özacar and Şengil, 2000), and removal of dyes, pigments and inks from ink-containing wastewater (Roussy et al., 2005). In these studies, coagulant such as aluminium sulphate was needed for destabilisation of the negatively charged colloidal particles, while anionic tannin acted as flocculant to bridge the destabilised aggregates together to form flocs of such a size suitable for sedimentation. A study showed that coupling of aluminium sulphate as coagulant and tannin as flocculant significantly reduced the required doses of the coagulant (Özacar and Şengil, 2003).

In order to eliminate the necessity of coagulant, modified tannin (Tanfloc flocculant) has been investigated recently to remove heavy metals from polluted surface water (Beltrán Heredia and Sánchez Martín, 2009) and in municipal wastewater treatment (Beltrán-Heredia and Sánchez-Martín, 2009). Tanfloc is obtained from *Acacia mearnsii* bark and modified by a physico-chemical process. Groups of hydrocolloid gums and other soluble salts are included in the Tanfloc structure with chemical modification which includes a quaternary nitrogen to give Tanfloc cationic character (Beltrán Heredia and Sánchez Martín, 2009). Due to its cationic property, it can be used for direct flocculation without coagulant and pH adjustment.

4.3. *Gums and mucilage*

Gums and mucilage have been proposed as a safer alternative to conventional polymers in wastewater treatment because its production process and applications which are environmental friendly and beneficial to human and ecology. Up to date, natural flocculants based on gums and mucilage that are derived from plant species include *Hibiscus/Abelmoschus esculentus* (Okra), *Malva sylvestris* (Mallow), *Plantago psyllium* (Psyllium), *Plantago ovata* (Isabgol), *Tamarindus indica* (Tamarind) and *Trigonella foenum-graecum* (Fenugreek) have been developed. These plant-based flocculants are generally obtained through aqueous extraction, precipitation with alcohol and drying (Fig. 3).

They have shown promising results with respect to treatment of landfill leachate (Al-Hamadani et al., 2011), biologically treated effluent (Anastasakis et al., 2009), textile wastewater (Mishra and Bajpai, 2005), tannery effluent (Mishra et al., 2004) and sewage effluent (Mishra et al., 2003). At least 85% of TSS removal, 70% of turbidity removal, 60% of COD reduction and 90% of colour removal have been reported in these studies. Some of them were effective in low concentrations and comparable to synthetic flocculants in terms of treatment efficiency. More than 85% removal of suspended solids from sewage wastewater and tannery effluent was achieved by using 0.12 mg/L of okra gum and 0.08 mg/L Fenugreek mucilage respectively, and the flocculation efficiency of these bio-flocculants was found at par with synthetic polyacrylamide (Agarwal et al., 2001; Mishra et al., 2004).

4.4. *Sodium alginate*

Sodium alginate, the sodium salt of alginic acid, with an average molecular weight of 500,000, is a linear water-soluble anionic polymer (Wu et al., 2012). A recent study investigated its flocculating efficiency in treatment of industrial textile wastewater and synthetic dye wastewater by using aluminium sulphate as the coagulant (Wu et al., 2012). The experimental

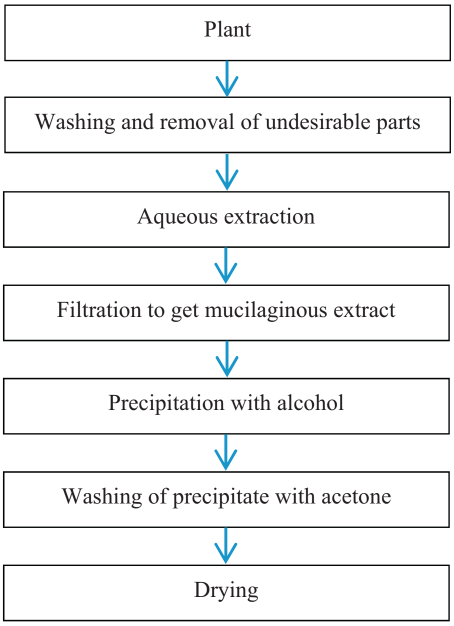

Fig. 3 – General processing steps in preparation of plant-based flocculants.

results revealed that it exhibited high flocculating property where more than 90% colour removal and 80% of COD reduction were obtained after treatment.

4.5. *Cellulose*

Cellulose is one of the most abundant natural polysaccharide. It has been the subject of research in recent years, mainly with respect to modify its physical and chemical structure by improving its properties and broadening its industrial applications (Das et al., 2012). Anionic sodium carboxymethylcellulose (CMCNa) that was prepared from an agricultural waste date palm rachis was tested as eco-friendly flocculants coupled with aluminium sulphate as coagulant for removal of turbidity in drinking water treatment (Khiari et al., 2010). In another study, anionized dicarboxylic acid nanocellulose (DCC) flocculant was produced and examined its flocculating property with ferric sulphate as coagulant in municipal wastewater (Suopajärvi et al., 2013).

4.6. *Challenges*

Even though bio-flocculants displayed promising flocculating efficiency in treatment of different types of wastewater but its future development is constrained by some disadvantages. Natural polymers have shorter shelf life because its active components will biodegrade with time and thus needs to be suitably controlled. Furthermore, the flocs tend to loose stability and strength with time because of their biodegradability. Most biodegradable natural and biopolymers contain hydrolysable groups along with the main chain which can cause biodegradation to happen via hydrolysis (Singh et al., 2000). In addition, some of the anionic bio-flocculants (e.g. tannin, cellulose, alginate) are moderately effective and only can be utilised as coagulant aid. In the coagulation–flocculation process, cationic coagulant is required for charge neutralisation before bio-flocculant could bridge the micro-flocs together and high dosage is needed to achieve efficient flocculation. Hence, in order to address all these concerns, new generation of polymeric flocculants has been developed by optimally grafting synthetic polymeric branches onto purified polysaccharide backbone (Pal et al., 2012).

5. Grafted flocculants/graft copolymers

The continuous increase of market needs for efficient and effective flocculants in wastewater treatment has induced the development of graft copolymers for flocculation of wastewater. Grafted materials thus have emerged as new materials that pose tremendous potential in treating wastewater due to its unique properties and superior performance compared to original components (conventional polymeric flocculants) (Lee et al., 2012). The modification of natural polysaccharides has been explored as a way of combining their best attributes with those of synthetic polymers and therefore enhance the aggregating power of flocculants by increase the ratio of effective component and positive electric charge of flocculants (Wang et al., 2008b).

Polysaccharides are fairly shear stable, in contrast with long chain synthetic polymers, and are biodegradable. However, they have lower efficiencies and thus higher concentrations or higher dosage are needed (Mishra et al., 2012). It is thus evident that all polymers, whether natural or synthetic, have one or another disadvantage. Many attempts have been made to combine the best properties of both by grafting synthetic polymers onto the backbone of natural polymers. Many grafted flocculants such as polymethylmethacrylate grafted psyllium (Psy-g-PMMA) (Mishra et al., 2014; Wang et al., 2009), polyacrylamide grafted starch (St-g-PAM) (Mishra et al., 2011), polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) (Pal et al., 2011), hydroxypropyl methyl cellulose grafted with polyacrylamide (HPMC-g-PAM) (Das et al., 2013) and poly(2-hydroxyethylmethacrylate) grafted agar (Rani et al., 2013) have been synthesised and their flocculating property was tested in synthetic wastewater (kaolin suspension) using Jar test procedure. The positive outcome of flocculation efficiency in pollutants removal suggested the possible application of these flocculants in wastewater treatment.

As presented in Table 7, many graft copolymers have been synthesised successfully by grafting polyacrylamide or poly(2-methacryloyloxyethyl) trimethyl ammonium chloride chains onto gums (Pal et al., 2011), chitosan (Wang et al., 2007), sodium alginate (Pal et al., 2012), celluloses (Das et al., 2013), starches (Sen et al., 2009), oatmeal (Bharti et al., 2013) and agar (Rani et al., 2012). The flocculating properties of the graft copolymers were examined in various types of wastewater treatment (e.g. pulp mill wastewater, municipal sewage wastewater, textile effluent, and raw mine wastewater) and found that their flocculating action depends on their molecular extensions in aqueous solution.

Further, by variation in the number and length of grafted polyacrylamide chains onto the backbone, it has been found that the graft copolymers have fewer and longer dangling polymer chains with high molecular weight and high branched structure. Such characteristics give easy approachability to contaminants in effluent and thus are claimed to be more efficient as flocculating agents at low dosage (Bolto and Gregory, 2007; Singh et al., 2000). The easy approachability model of flocculation (Brostow et al., 2007; Singh et al., 2000) showed that the presence of grafted polyacrylamide chains would enhance the hydrodynamic volume (i.e. radius of gyration) of a polymer in solution, and thereby increasing its flocculation ability. Some research works revealed that graft

Table 7 – Application of grafted flocculants in wastewater treatment.

Coagulant(s)	Flocculant(s)	Type of wastewater	Optimum results		Reference
Aluminium chloride	Chitosan grafted PDMC (poly(2-methacryloyloxyethyl) trimethyl ammonium chloride)	Paper recycling wastewater	Turbidity	687–8.7NTU	Wang et al. (2007)
Aluminium chloride	(2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC) grafted chitosan (cationic)	Pulp mill wastewater	Turbidity	99.4% removal	Wang et al. (2009)
			Lignin	81.3% removal	
			COD	90.7% removal	
–	Polyacrylamide grafted carboxymethylstarch (CMS-g-PAM)	Municipal sewage wastewater	Turbidity	20–4NTU	Sen et al. (2009)
			TS	602–356 ppm	
–	Hydrolysed polyacrylamide grafted carboxymethylstarch (Hyd. CMS-g-PAM)	Textile industry wastewater	Turbidity	97–54NTU	Sen et al. (2011)
			TS	640–309 ppm	
			COD	586–221 ppm	
Aluminium chloride	Starch-g-PAM-g-PDMC [polyacrylamide and poly (2-methacryloyloxyethyl) trimethyl ammonium chloride]	Pulp mill wastewater	Turbidity	99.6% removal	Wang et al. (2011)
			Lignin	88.4% removal	
			Water recovery	74% removal	
–	Polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM)	Municipal sewage wastewater	Turbidity	64–9NTU	Pal et al. (2011)
			TS	630–230 ppm	
			COD	540–210 ppm	
			Fe^{3+}, Mn^{2+}, Cr^{2+}, Ni^{2+}	Almost 100% removal	
		Dye solution	COD	63.5% removal	
–	Carboxymethylstarch grafted polyacrylamide, tamarind kernel polysaccharide grafted polyacrylamide, sodium alginate grafted polyacrylamide (nonionic or slightly anionic)	Municipal sewage wastewater	COD	540–205 ppm	Pal et al. (2012)
			TSS	335–55 ppm	
			Fe^{3+}, Mn^{2+}, Cr^{2+}, Ni^{2+}	Nearly 100% removal	
–	Hydroxypropyl methyl cellulose grafted with polyacrylamide (HPMC-g-PAM)	Raw mine wastewater	Turbidity	386.5–25.3NTU	Das et al. (2013)
			TS	928.7–167.5 ppm	
			COD	364.2–112.6 ppm	
–	Carboxymethyl chitosan grafted polyacrylamide (CMC-g-PAM)	Dye solution	Anionic dye (methyl orange)	93% removal	Yang et al. (2013)
			Cationic dye (basic bright yellow)	95% removal	
			Al^{3+}	85.8% removal	
			COD	90.4% removal	
–	Polyacrylamide grafted oatmeal (OAT-g-PAM)	Municipal sewage wastewater	Turbidity	63–28NTU	Bharti et al. (2013)
			TS	500–100 ppm	
–	Polyacrylamide grafted agar	Municipal wastewater	TSS	220–79.5 ppm	Rani et al. (2012)
			COD	418–186 ppm	

copolymers showed superior flocculation characteristics in turbidity removal when compared with commercially available flocculants (Pal et al., 2005; Singh et al., 2006; Wang et al., 2008a).

Another great advantage of grafted flocculant is the consequent reduced biodegradability because of the drastic change in the original regular structure of the natural polymer as well as the increased synthetic polymer content in the product. The graft copolymers are found less susceptible to biodegradation because grafting promotes alteration of structure of polysaccharide molecules and thus will make it less suitable as a substrate for enzymatic degradation. Moreover, the inert polyacrylamide content also increases with grafting polysaccharides, making it less prone to biological attack and more biodegradable resistant (Singh et al., 2000). It is also observed that grafting of shear degradable polymers onto the rigid polysaccharide backbone provides fairly shear stable systems (Singh et al., 2000).

In principle, cationic organic flocculants should be more effective in dealing with negatively charged contaminants or particle suspensions, such as clay and dye. Therefore, cationic flocculants have been synthesised by incorporating a cationic moiety N-(3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) onto the backbone of guar gum (Singh et al., 2006) or starch (Pal et al., 2005; Pal et al., 2008) in presence of sodium hydroxide. These studies showed that the cationic flocculants with longer CHPTAC chains showed better flocculation performance compared with commercially available flocculants in suspension containing negatively charged particles.

However, some wastewater such as textile effluent is complicated and may contain undesirable cationic and anionic colloidal particles. Therefore, it was proposed that amphoteric flocculants containing both cationic and anionic ions could eliminate both cationic and anionic contaminants. In recent years, amphoteric chitosan-based flocculants have been synthesised and their flocculating characteristics have been evaluated using kaolin suspension as synthetic wastewater (Yang et al., 2012a,b), raw water from river (Yang et al., 2012a), and dye-containing solution (Yang et al., 2013). It was noticed that amphoteric chitosan copolymer showed higher removal efficiency compared to chitosan and produced notably more compacted flocs.

In short, grafting is the most effective way of regulating the properties of polysaccharides which can be ‘tailor-made’ according to the needs and produce high efficient graft copolymers. However, the main problem in the case of graft copolymers is the lack of commercial methods of synthesis (Mishra et al., 2011). The chief methods of synthesis of grafted polysaccharides involve the use of chemical free radical initiator (conventional method), high energy radiations (gamma and X-ray), UV-radiation based method and microwave based methods.

The conventional method of synthesis uses a chemical free radical initiator (e.g. ceric ammonium nitrate or CAN) to generate free radical sites on the backbone polymer, where the monomer of the graft gets added up to form the graft chain (da Silva et al., 2007; Sen et al., 2009). This method of synthesis has low reproducibility and is not suitable for commercial scale synthesis. A better method of graft copolymer synthesis is by using high energy radiation (gamma rays or electron beam) as the free radical generator (Vahdat et al., 2007; Wang et al., 2008a) but this method can cause damage to the polysaccharide backbone (radiolysis). UV rays in presence of suitable photosensitizor can also be used, but low penetration of UV-rays makes it suitable for surface grafting only.

Up to now, the best method of graft copolymer synthesis is by use of microwave radiation to generate the free radical sites on the backbone polymer (Mishra et al., 2011) but this method is associated with high production cost. As a summary, more researches are needed to discover an environmental friendly and economic feasible method for synthesis of high quality grafted flocculants which exhibit excellent capability in pollutants removal and these modified products can be further exploited for the treatment of many industrial effluents.

6. Selection of flocculants

After understanding the treatment processes including coagulation–flocculation and direct flocculation and different types of flocculants, the task to achieve the desired clarification or purification will be much easier. Based on literature work, the flocculants that have been used for treatment of different types of wastewaters are compiled and presented in Table 8. For any wastewater treatment, the first step is to examine the characteristics of the wastewater where it will determine the selection of treatment process. As presented in Table 3, coagulation–flocculation is normally suitable for any kind of wastewaters that contain suspended and dissolved constituents while direct flocculation is only applicable to treat organic-based effluents that contain suspended solids.

The next move is to choose the type of flocculant(s) to be used. As the surface charge of the colloidal suspensions is generally negative, thus cationic coagulant or flocculant is always elected. For coagulation–flocculation process, cationic coagulant is commonly coupled with non-ionic or anionic flocculants. On the other hand, cationic or anionic flocculants are usually selected for direct flocculation process. There is a wide variety of flocculants available in the market with different molecular weight and charge density. Normally, high molecular weight flocculants are preferable because it is associated with bridging mechanism which is stronger compared to other flocculation mechanisms.

7. Flocculation mechanisms

Generally, development of flocs formation involves several steps occurring sequentially:

(a) Dispersion of the flocculant in the solution.
(b) Diffusion of the flocculant towards the solid-liquid interface.
(c) Adsorption of the flocculant onto the surface of the particles.
(d) Collision of particles carrying an adsorbed flocculant with other particles.
(e) Adsorption of the flocculant onto other particles in order to form microflocs.
(f) Growth of the microflocs to larger and stronger flocs by successive collision and adsorption.

Several flocculation mechanisms such as polymer bridging, polymer adsorption and charge neutralisation (including electrostatic patch effects), depletion flocculation, displacement flocculation, etc. have been proposed to explain the destabilisation of colloids and suspensions by polymers and the mechanism of flocs formation (Bolto and Gregory, 2007;

Table 8 – Selection of flocculants based on different wastewaters.

Industry area	Type of wastewater	Treatment process	Coagulant (commonly is cationic)	Cationic flocculant	Neutral flocculant	Anionic flocculant	Reference
Food and beverage	Coffee wastewater	C-F	√	–	–	√	Zayas Péerez et al. (2007)
	Beverage wastewater	C-F	√	–	√	–	Amuda and Amoo (2007)
	Sauce wastewater	C-F	√	–	–	√	Martín et al. (2011)
Paper	Pulp and paper mill wastewater	C-F	√	√	–	√	Ahmad et al. (2008), Irfan et al. (2013) and Rodrigues et al. (2008)
		D-F	–	√	–	√	Razali et al. (2011) and Wong et al. (2006)
	Ink-containing effluent	C-F	√	–	–	√	Roussy et al. (2005)
	Cardboard industry wastewater	D-F	–	√	–	–	Renault et al. (2009a,b)
Agricultural production	Palm oil mill effluent	C-F	√	–	–	√	Ahmad et al. (2005)
	Aquaculture wastewater	D-F	–	√	–	–	Ebeling et al. (2005)
	Olive mill effluent	C-F	√	√	–	√	Ginos et al. (2006)
		D-F	–	√	–	√	Ginos et al. (2006) and Sarika et al. (2005)
	Abattoir wastewater	C-F	√	–	–	√	Amuda and Alade (2006)
Dye/textile	Dye-containing/textile wastewater	C-F	√	–	–	√	Joo et al. (2007) and Wu et al. (2012)
		D-F	–	√	–	–	Kang et al. (2007), Szyguła et al. (2009) and Yue et al. (2008)
Municipal	Sewage effluent	D-F	–	–	–	√	Mishra et al. (2002)
	Municipal wastewater	C-F	√	–	–	√	Suopajärvi et al. (2013)
		D-F	–	√	–	–	Beltrán-Heredia and Sánchez-Martín (2009)
Others	Tannery effluent	D-F	–	–	√	√	Mishra et al. (2002) and Mishra et al. (2004)
	Ceramic wastewater	D-F	–	√	–	√	Chong et al. (2009)
	Polymer effluent	C-F	√	–	–	√	Sher et al. (2013)

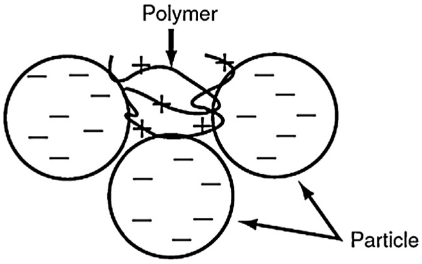

Fig. 4 – Schematic view of a charge neutralisation flocculation mechanism (Bohuslav Dobias, 2005).

Renault et al., 2009a). The main mechanisms of coagulation/flocculation involved in the removal of dissolved and particulate contaminants which are often cited are charge neutralisation, bridge formation and electrostatic patch. These mechanisms are crucially dependent on the adsorption of flocculants on particle surfaces (Bolto and Gregory, 2007). If there is some affinity between polymer segments and a particle surface, then adsorption of polymer chains may occur.

7.1. *Mechanism for chemical flocculants*

7.1.1. *Charge neutralisation*

For the case where the flocculant and the adsorption site are of opposite charge, generally charge neutralisation is postulated as the major mechanism. In many practical cases, hydrophobic colloidal particles in wastewater are negatively charged and thus inorganic flocculants (metal salts) and cationic polyelectrolytes are preferable. The flocculation could occur simply as a result of the reduced surface charge of the particles (reduction of zeta potential) and hence a decreased electrical repulsion force between colloidal particles, which allows the formation of van der Waals force of attraction to encourage initial aggregation of colloidal and fine suspended materials to form microfloc (Fig. 4).

In many studies, it has been found that optimum flocculation occurs at polyelectrolytes dosages around that needed to just neutralise the particle charge, or to give a zeta potential close to zero (isoelectric point). At this point, the particles would tend to agglomerate under the influence of the Van der Waals' forces and the colloidal suspension becomes destabilised (Kleimann et al., 2005). If too much polymer is used, however, a charge reversal can occur and the particles will again become dispersed, but with a positive charge rather than negatively charged. Sometimes, the flocs formed with charge neutralisation are loosely packed and fragile and settle slowly. Thus, addition of another high molecular weight polymer with bridging effect is necessary to bond the microflocs together for fast sedimentation and high water recovery (Ahmad et al., 2008).

7.1.2. *Polymer bridging*

In general, polymer bridging occurs when long chain polymers with high molecular weight (up to several million) and low charge density (Caskey and Primus, 1986) adsorbed on particles in such a way that long loops and tails extending or stretching some way into solution far beyond the electrical double layer (Fig. 5a). This gives the possibility attachment and interaction of these 'dangling' polymer segments to other particles, thus create 'bridging' between particles as shown in Fig. 5(b) (Biggs et al., 2000; Blanco et al., 2002; Lee et al., 2012).

For effective bridging to occur, the length of the polymer chains should be sufficient to extend from one particle surface to another. Hence a polymer with longer chains (high molecular weight) should be more effective than one with shorter chains (low molecular weight) (Razali et al., 2011). Besides, there should be sufficient unoccupied surface on a particle for attachment of segments of polymer chains adsorbed on other particles. It follows that the amount of polymer should not be excessive (adsorbed amount should not be too high), otherwise the particle surfaces will be overly coated with polymer such that no sites are available to 'bridge' with other particles (Sher et al., 2013). Here the particles are said to be restabilised as shown in Fig. 5(c).

Thus, there is only a limited adsorbed amount of polymer is needed and excess levels can give restabilisation. Of course, the adsorbed amount should not be too low; otherwise not enough bridging contacts could be formed. These considerations lead to the idea of an optimum dosage for bridging flocculation (Bolto and Gregory, 2007). It is well established that polymer bridging can give much larger and stronger

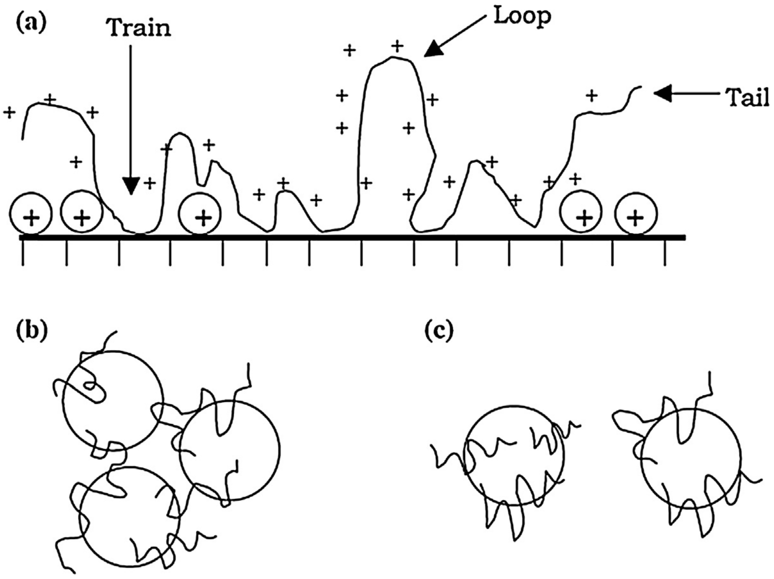

Fig. 5 – (a) Adsorption of polymer and formation of loops available for binding. (b) Polymer bridging between particles (aggregation). (c) Restabilisation of colloid particles (floc breakup) (Sharma et al., 2006).

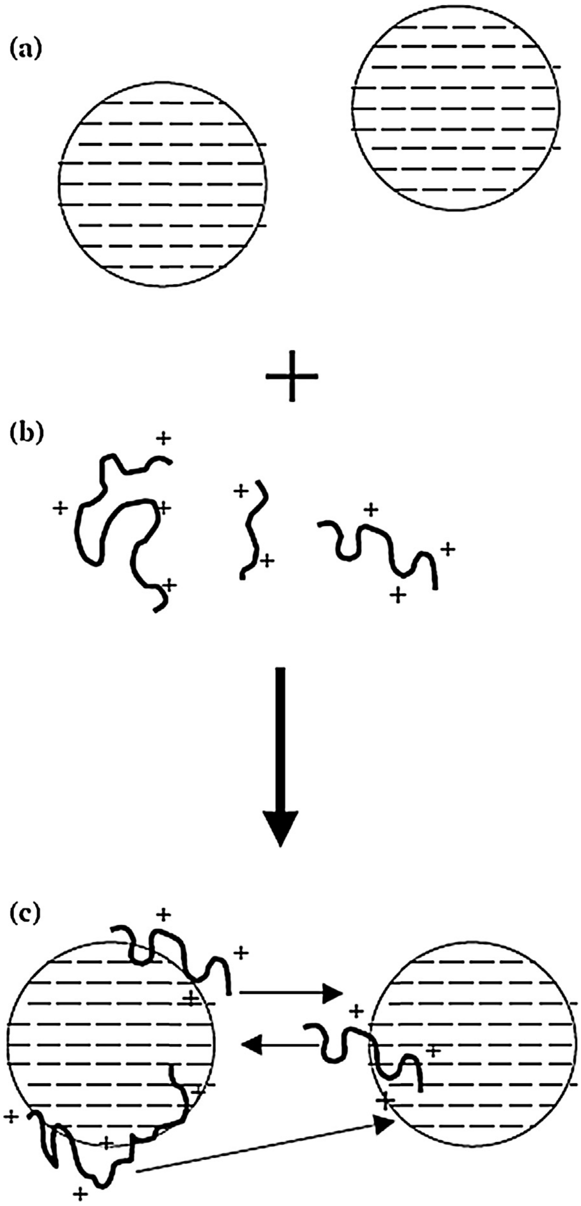

Fig. 6 – (a) Negatively charged particles. (b) Cationic flocculants. (c) Charge neutralisation flocculation by patch mechanism. Arrows in (c) show attraction of opposite charges (Sharma et al., 2006).

aggregates (flocs) than those formed in other ways. In addition, bridging contacts are also more resistant to breakage at elevated shear levels.

7.1.3. *Electrostatic patch*

When high charge density polyelectrolytes with low molecular weight adsorb on negative surfaces with a fairly low density of charged sites, bridging capability is reduced and another possibility arises, which is known as 'electrostatic patch' mechanism. The basic idea is that, when a highly charged cationic polymer (Fig. 6b) adsorbs on a weakly charged negative surface (Fig. 6a), to give overall neutrality, it is not physically possible for each surface charged site to be neutralised by a cationic polymer segment (Blanco et al., 2002). There is formation of cationic 'patches' or 'islands' between regions of uncoated, negatively charged surfaces.

An important consequence of 'patchwise' adsorption is that, as particles approach closely, there is an electrostatic attraction between positive patches and negative areas, which can give particle attachment and hence flocculation (Fig. 6c) (Bolto and Gregory, 2007). Flocs produced in this way are not as strong as those formed by bridging, but stronger than flocs formed in the presence of metal salts or by simple charge neutralisation. The charge density of polyelectrolytes needs to be quite high for efficient electrostatic patch flocculation. As the charge density is reduced, bridging flocculation becomes more likely (Eriksson et al., 1993).

7.2. *Mechanism for natural bio-flocculants*

The properties of chitosan, including its cationic behaviour (reactive amino and hydroxyl groups) and high molecular weight, may be used for both coagulation by charge neutralisation and flocculation by bridging mechanism (Li et al., 2013). In a study that investigated coagulation and flocculation of dye-containing solutions using the chitosan, the anionic dye was electrostatically attracted by protonated amine groups from chitosan leading to neutralisation of the anionic charges of dyes and then the flocculation was further enhanced by the bridging mechanism which bind the agglomerates together and settle (Guibal and Roussy, 2007). The behaviour of chitosan involves two factors, namely hydrophobic interactions and the possibility of chain association through hydrogen bridges (Szyguła et al., 2009), depending on the nature of the colloids, characteristics of chitosan such as molecular weight and degree of deacetylation, the pH of the suspension and the experimental conditions (i.e., concentrations).

For anionic bio-flocculants (cellulose, tannin and sodium alginate), they are unable to flocculate anionic contaminants from the wastewater without the assistance from a cationic coagulant/flocculant. Therefore, addition of inorganic metal salts (e.g. aluminium and ferric salts) or cationic polymer (e.g. chitosan) before addition of bio-flocculant is necessary for charge neutralisation of negatively charged impurities (Khiari et al., 2010; Özacar and Şengil, 2003; Roussy et al., 2005; Suopajärvi et al., 2013; Wu et al., 2012). After charge neutralisation, anionic cellulose or tannin with negatively charged backbone (carboxyl and hydroxyl groups) allowed the polymer molecules to be extended into solution and produce loops and tails to promote bridging of flocs (Suopajärvi et al., 2013).

It was interesting to notice that most of the mucilage extracted from plants (plant-based bio-flocculants) is either anionic or non-ionic, and they can be used in wastewater treatment without addition of coagulant (direct flocculation). For the study that investigated the flocculation behaviour of textile wastewater treated with *Plantago psyllium* mucilage (Mishra and Bajpai, 2005) and *Tamarindus indica* mucilage (Mishra and Bajpai, 2006), polymer bridging was proposed as the plausible mechanism. For other bio-flocculants (Mallow and Tamarind mucilage) where the surface charge is unknown or unidentified, its flocculation mechanism is difficult to be predicted and has not been literally discussed with research findings.

7.3. *Mechanism for grafted flocculants/graft copolymers*

The flocculation mechanism for grafted flocculants involved in wastewater treatment is a combination of charge neutralisation and polymer bridging (Pal et al., 2011; Song et al., 2011; Yang et al., 2012a, 2013). Charge neutralisation predominates at the beginning of the flocculation process and produces numbers of insoluble complexes with a rapid speed. Then,

Table 9 – Flocculation mechanism for different types of flocculants.

Category of flocculants	Type of flocculant	Flocculation mechanism
Chemical coagulants	Inorganic metal salts	Charge neutralisation
Chemical flocculants	Polyelectrolytes with low MW and low CD Polyelectrolytes with high MW and low CD Polyelectrolytes with low MW and high CD Polyelectrolytes with high MW and high CD	Charge neutralisation Bridging Electrostatic patch Electrostatic patch + bridging
Bio-flocculants	Cationic chitosan Anionic cellulose and tannin and sodium alginate Anionic/neutral plant-based flocculants	Charge neutralisation + bridging Bridging Bridging
Grafted flocculants	Amphoteric/cationic/anionic graft copolymers	Charge neutralisation + bridging/bridging only

Table 10 – Case studies about flocculation mechanism.

Type of flocculant	Characteristics of flocculant	Flocculation medium	Flocculation mechanism	Reference
Quaternary ammonium based derivative of polyacrylamide (cationic)	High MW (16×10^6), high CD (100%)	Colloidal dispersion of anionic polystyrene latex particles	Bridging	Biggs et al. (2000)
Cationic polyacrylamide (C-PAM)	High MW, low CD	Suspension of calcium carbonate	Bridging	Blanco et al. (2002)
Polyethyleneimine (cationic)	Low MW, high CD		Electrostatic patch	
PolyDADMAC (cationic)	Medium MW, medium CD		Charge neutralisation	
Cationic copolymers of acrylamide/ diallyldimethylammonium, chloride	Medium MW (3×10^5), low CD (10%)	Suspension of silica particles	Bridging	Zhou and Franks (2006)
	Medium MW (1.1×10^5), medium CD (40%)		Charge neutralisation + bridging/bridging	
Cationic homopolymer of diallyldimethylammonium chloride	Medium MW (1.2×10^5), high CD (100%)		Electrostatic patch	
Cationic polyacrylamide (C-PAM)	High MW, low CD	Suspension of calcium carbonate	Bridging	Rasteiro et al. (2007)
	High MW, high CD		Electrostatic patch	
Cationic polyacrylamide (C-PAM)	High MW (7.2×10^6), high CD (80%)	Suspension of calcium carbonate	Electrostatic patch + bridging	Rasteiro et al. (2008)
	High MW (13×10^6), medium CD (50%)		Bridging	

through bridging effect due to the flexible polymeric graft chains, the insoluble complexes aggregate and form larger net-like flocs. Finally, the compacted flocs are formed and settled down rapidly (Yang et al., 2013).

Other research works revealed that bridging is the leading flocculation mechanism (Das et al., 2013; Pal et al., 2011). The reason for better flocculation characteristics of graft copolymers over linear polymer is essentially due to polymer bridging mechanism. Segments of the polymer chain adsorbed onto different particles surface, forming bridges between adjacent particles and finally linked all the particles together. The length of the polymer chains of grafted flocculants are longer and the radius of gyration is higher, thus the adsorbed polymer molecules tend to adopt more extended configuration for interacting with more than one particle.

7.4. *Summary of flocculation mechanism for different types of flocculants*

The flocculation mechanism for different types of flocculants could be summarised in Table 9. In addition, some case studies have been conducted to investigate the underlying mechanism behind the flocculation process induced by chemical polymeric flocculants by using Light Diffraction Scattering (LDS) technique. As shown in Table 10, it is clear that molecular weight and the charge density play the important role to influence and decide the acting mechanism.

In order to control and optimise the flocculation process, it is highly important to know and understand the flocculation mechanism during the whole process. However, the investigation and discovery of the underlying mechanism for removal of impurities or contaminants from wastewater with bio-flocculants and grafted flocculants is still lacking and immature.

8. Conclusion and future perspectives

The potential application of conventional flocculants, bio-flocculants and grafted flocculants in wastewater treatment has been verified and well investigated. They have shown remarkable results in reduction or removal of environmental concerned parameters such as TSS, turbidity, COD and colour with more than 90% removal was achieved in some of the studies. Although many flocculating materials have been developed and successfully used in removing pollutants from wastewater in laboratory scale, there is still a need to improve their performance in removal of suspended and dissolved impurities, heavy metals, and colour or dye molecules, inorganic or organic pollutants in order to meet the environmental legislation before the wastewater is discharged to the environment. Considering the industrial dependencies on the cost effective flocculation technology for wastewater treatment, it is required to conduct more future research for best flocculants which is capable to produce very promising results in pollutants removal even at wider variations of pH and other contaminants of the wastewater.

For chemical flocculants, the flocculation optimisation practices in the industry are still scarce because of the highly complex nature of the flocculation process and the large variety of polyelectrolytes available. One of the ways to optimise the flocculation process is by selecting or controlling the range of the molecular weight and the charge density of the polymer. Different molecular weights and charge density produce different flocculation mechanisms (neutralisation or bridging). Future research needs to look into how molecular weight and charge density distribution affect the flocculation performance to produce a better choice of flocculants for specific industrial applications. Optimisation of these factors could significantly increase the treatment efficiency and reduce the chemical cost.

Since the usage of conventional flocculants is closely related with environmental pollution and health hazards, synthesis of environmental friendly and economic viable flocculants that exhibit high flocculating efficiency is highly desirable. As discussed above, some of the developed bio-flocculants or grafted flocculants displayed promising flocculating ability, where more than 90% reduction of TSS, turbidity, COD and colour was observed in treatment of various types of wastewaters. However, the development of bio-flocculants or grafted copolymers is only at very beginning state and constrained by many uncertainties such as unknown production cost and non-standardised production process. Nevertheless, a cost–benefit analysis of using bio-flocculants for this purpose and optimisation study to generate a standard protocol of production and maximise the flocculating efficiency needs to be conducted to judge the economic feasibility of its practical use.

In addition, very limited work has been carried out on the industrial scale, mostly is concentrated in laboratory testing. The complexity of the coagulation and flocculation systems justifies that a polymer cannot be selected for a given application without experimental testing. This testing involves two stages: (i) laboratory tests for selecting the type of flocculants and more particularly the optimum ionicity and (ii) industrial trials or practices for confirming the flocculant selection and for determining its amount and its molecular weight. Thus, the applicability and the effectiveness of most of the bio-flocculants for wastewater treatment are yet to be established. Investigation on the effectiveness of more natural flocculants is also required.

At last but not least, the selection of high efficient flocculants that could nearly remove or reduce all of the contaminants in wastewater is essential for a successful flocculation process. Environmental friendly flocculants that can be produced by simple and economically viable process which exhibits high removal efficiencies and considerably denser flocs is regarded as a promising material in real application from the perspective of both performance and cost.

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