Review of Utilization Plant-Based Coagulants as Alternatives to Textile Wastewater Treatment

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Abstract With the increased demand for textile products, the textile industry and its wastewaters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide. Textile wastewater treatment is one the most difficult environmental problems because it contains high color, biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, temperature, turbidity and toxic chemicals. The direct discharge of this wastewater without previous or proper treatment into the water bodies, like lakes, rivers, etc. pollutes the water affecting directly and indirectly the water. Coagulation/flocculation is one of the most widely used for wastewater treatment, as it is efficient and simple to operate. This process is used for the removal of suspended and dissolved solids, colloids and organic matter present in industrial wastewater. Natural coagulants have been attracting wide interest of researchers because they have the advantages of biodegradability, safe for human health, environmental friendly, generally toxic free and produce no secondary pollution. These coagulants are extracted from natural and renewable sources, such as microorganisms, animals or plants. Not only this, the sludge volume generated by the natural coagulants is smaller than chemical coagulants; it can further be treated biologically or can be disposed safely as soil conditioners because of their non-toxicity. The raw plant extracts are often available

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locally and hence, a low-cost alternative to chemical coagulants. In recent years, numerous studies on natural coagulants are growing and there is an urgent need to establish the use of natural low-cost coagulants for textile wastewater treatment. In this chapter, we show the characteristics of dyes and textile wastewater, emphasizing adverse impacts on environmental and human health and we mentioned some technologies for the textile wastewater treatment, highlighting the CF, since it is efficient, is easy to operate and is commonly used at the industries. We also have been discussed the physical-chemical concept of CF as well the major mechanisms involved at process. The usage of plant-based natural coagulants as alternative to chemical coagulants in the textile wastewater treatment is the goal of this chapter.

Keywords Natural coagulant · Plant coagulant · Coagulation/flocculation · Textile treatment · Textile effluent

List of Abbreviations

ANOVA	Analyses of variance
BOD	Biochemical oxygen demand
CF	Coagulation/flocculation process
COD	Chemical oxygen demand
OD	Oxygen dissolved
PAC	Polyaluminium chloride
POPs	Persistent organic pollutants
TCD	Textile contact dermatitis
TDS	Total dissolved solids
TDSO	Tumorigenic dose rate 50
TOC	Total organic carbon
TSS	Total suspense solids
USEPA	Environmental Protection Agency

1 Textile Wastewater

Environmental pollution is currently one of the most important issues faced by humanity. Pollution has increased exponentially in the past few years and has reached alarming levels in terms of its effects on living creatures (Prasad and Rao 2016). Increase in demand for rapid urbanization and changing consumption patterns, together with unrestrained population growth, rapid socioeconomic development and changes in agriculture, medicine, energy sources, and chemical industries have all resulted in the generation of environmental pollutants. These pollutants are released into air, water, and soil and have detrimental effects on the health of humans, plants, animals, and microbes (Ali 2010; Colpini et al. 2014; Souza et al. 2016; Uday et al. 2016).

The textile industry is one of the most important manufacturing sectors and produces large volumes of highly toxic wastewater due to the high quantities of water, dyes and chemicals used in its processes (Jegatheesan et al. 2016; Gümüş and Akbal 2011). The World Bank estimates that 17–20% of industrial water pollution is contributed by the textile industry (Kant 2012; Jegatheesan et al. 2016).

Scouring, dyeing, printing, finishing and washing processes contribute the highest volumes of wastewater (Dasgupta et al. 2015). The traditional textile finishing industry consumes about 100 L of water per 1 kg of textile materials (Ali 2010). The dyeing industry consumes about 30–50 L of water per 1 kg of cloth depending on the type of dye used. The overall water consumption of yarn dyeing is about 60 L per 1 kg of yarn (Kant 2012). In general, textile industries typically generate 200–350 L of wastewater per 1 kg of finished product (Gozálvez-Zafrilla et al. 2008) resulting in an average pollution of 100 kg chemical oxygen demand (COD) per ton of fabric (Jekel 1997). For a textile unit processing 400,000 lb of cotton per week, more than 50,000 lb of salts are released. The usual salt concentration in wastewater is 2000–3000 ppm (Khandegar and Saroha 2013). The salts in the effluent can lead to the soil infertility and aquatic life damage (Khandegar and Saroha 2013). Not to mention that about 2 to 50% of the total dyes that have not been fixed to the fiber are lost during dyeing and washing process, leading to severe contamination of surface and ground water (O'Neill et al. 1999).

The Environmental Protection Agency (USEPA) has classified textile wastes into four principal groups, namely dispersible, hard-to-treat, high-volume, and hazardous and toxic wastes (Foo and Hameed 2010). The composition and volume of wastewater from textile industries exhibit wide heterogeneity, depending on many different factors, including the type of fibers, chemicals and dyes, machines, techniques, the season of the year, the characteristic quality imparted to processed fabric, the nature of the special finishing if any, the specificity of the process and the principles on which the water use has been modeled (Santos et al. 2007; Dasgupta et al. 2015; Soares et al. 2017).

In general, textile wastewater is quite a complex mixture and is highly variable, comprising many polluting substances. It is a mixture of different types of dyes and auxiliary products such as surfactants, fixing agents, oxidizing agents, recalcitrant chlorinated compounds, salts, heavy metals, dispersing agents and smoothing agents (compounds that may be both persistent and toxic) (Hassani et al. 2008; Zahrim et al. 2011). Wastewaters are highly colored due to the presence of dyes that have not been fixed to the fiber during the dyeing process (Kunz et al. 2002). They are usually also characterized by high levels of chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, salinity, temperature, turbidity, toxic chemical compounds, total dissolved solids (TDS) and total suspended solids (TSS) (Valh et al. 2011; Verma et al. 2012). Furthermore, many textile dyes or by-products are themselves toxic, carcinogenic, mutagenic and/or teratogenic (Mathur et al. 2005; Khandegar and Saroha 2013; Santos et al. 2013). Table 1 lists the characteristics of textile wastewaters from different stages of textile industry processes, and wastewater discharge standards prescribed by the statutory authorities.

Table 1 Physical-chemical characteristics of textile wastewater from textile processing (Santos et al. 2007; Valh et al. 2011; Khandegar and Saroha 2013; Arslan et al. 2016)

Parameters	General industry	Scouring	Bleaching	Mercerising	Dyeing	Composite	Desizing	Discharge limit into public sewage (Indian legislation)	Discharge limit into water (Brazilian legislation)	Discharge limit into water and municipal wastewater treatment plan (China legislation)	
										Direct	**Indirect**
pH	1.9–13	10–12	8.5–11	8–10	9–11	8–10	–	5.6–9.0	5.0–9.0	6.0–9.0	6.0–9.0
TDS (mg L^{-1})	2900–3100	12,000–30,000	2500–11,000	2000–2600	1500–4000	5000–10,000	16,000–32,000	2100	–	–	–
TSS (mg L^{-1})	15–64,000	1000–2000	200–400	100–400	50–350	100–700		100	–	60	100
BOD_5 (mg L^{-1})	50–40,000	2500–3500	100–500	50–120	100–400	50–550	1700–5200	30	50	25	50
COD (mg L^{-1})	150–12,000	10,000–20,000	1200–1600	250–400	400–1400	250–8000	4600–5900	250	200	100	200
Color	50–2500 (mgPtCo L^{-1})	–	–	Highly colored	Strongly colored	Strongly colored	–	Colorless	75 (mgPtCo L^{-1})	70 (dilution ratio)	80 (dilution ratio)

COD: chemical oxygen demand, BOD_5: biochemical oxygen demand incubated to 5 days, mgPtCo L^{-1}: milligrams Platinum-Cobalt per liter, TDS: total dissolved solids, TSS: total suspended solids

*Brazilian legislation, Conama Resolution n° 430/2011 and CEMA Resolution n° 70/2009; China legislation, GB 4287-2012; Bureau of Indian Standards, BIS-3306-1955

2 Textile Dyes

Colorants (dyes and pigments) are important industrial chemicals. Pigments are colorants which are insoluble in water and do no interact with the substrates, whereas dyes are mostly soluble in water and diffuse into the material and are fixed to colorize the material (Chequer et al. 2011; Uday et al. 2016). Textile dyes are organic compounds that give color to fibers (substrate). Although in chemistry, "dye" denominates only substances of aromatic character that are capable of irreversibly coloring a textile support, the term "dye" can refer to any substance that gives color, including both dyes and paints (Moraes et al. 2000; Dellamatrice et al. 2008).

There are different types of classifications for dyes. They can be classified in terms of their chemical structure, color and application methods. However, due to the complexities of color nomenclature based on the chemical structure system, classification based on the application is often favorable (Guaratini and Zanoni 2000; Yagub et al. 2014). Fibers can take up dyes as a result of van der Waals forces, hydrogen bonds and hydrophobic interactions. The uptake of the dye into fibers depends on the nature of the dye and its chemical constituents. The strongest dye-fiber attachments are as a result of covalent bonds with additional electrostatic interactions where the dye ions and the fibers have opposite charges (Santos et al. 2007). Thus, knowing the nature of the fiber is important because the fiber structure determines the kind of dye that should be used and application method (Moura 2003). Figure 1 shows the main types of dyes used for dyeing different kinds of fiber and Table 2 represents the characteristics of different dyes that are used widely in the textile industry. It can be seen in Table 2 that reactive dyes are widely used to color cotton, which contributes half of the worldwide textile-fiber market (Verma et al. 2012).

Dyes are also classified based on their chemical structure and they are constituted by two main groups, chromophores and auxochromes (based on their functional groups). Figure 2 illustrates the chemical structure of dye molecules. Chromophore groups are characterized by the presence of a delocalized electron system with conjugated double bonds (π-π^* and n-π^* transitions) in the molecular

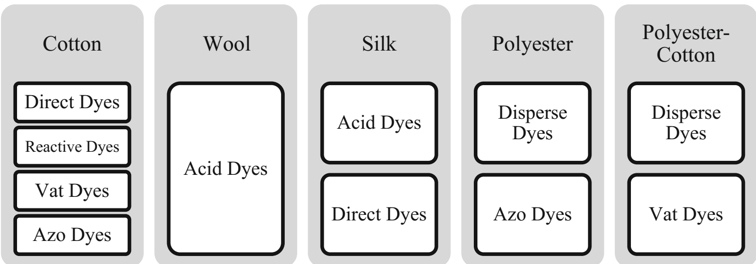


Fig. 1 Dyes for different fibers. Reprinted from Holkar et al. (2016) with permission of Copyright © 2016 Elsevier Ltd.

Table 2 Classification of dyes mainly used in textile industry and its method of application (O'Neill et al. 1999; Guaratini and Zanoni 2000; Hunger 2007; Verma et al. 2012; Yagub et al. 2014)

Class	Characteristics	Substrate (Fiber)	Dye-fiber interaction	Application method	Chemical types	Degree of fixation (%)	Loss to effluent (%)
Acid	Anionic, water soluble	Wool, nylon, silk	Electrostatic, Hydrogen bonding	Generally from neutral to acidic dyebath	Anthraquinone, azine, xanthene, azo (including, nitroso, premetallised), nitro, triphenylmethane, xanthene	89–95	5–20
Basic	Cationic, water soluble	polyacrylonitrile, treated nylon, and polyester	Electrostatic attraction	Applied from acidic dyebaths	Hemicyanine, azo, cyanine, azine, diazahemicyanine, diphenylmethane, xanthene, acridine, triarylmethane, anthraquinone, oxazine	95–100	0–5
Direct	Anionic, water soluble	Nylon, rayon, leather and cotton	Intermolecular forces	Applied from neutral or a little alkaline bath containing additional electrolyte	Phthalocyanine, azo, oxazine, stilbene	70–95	5–30
Disperse	Very low water solubility	Polyamide, acrylic polyester and acetate	Hydrophobic-solid state mechanism	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and thermo fixed	Benzodifuranone, azo, anthraquinone, nitro, styryl	90–100	0–10

(continued)

Table 2 (continued)

Class	Characteristics	Substrate (Fiber)	Dye-fiber interaction	Application method	Chemical types	Degree of fixation (%)	Loss to effluent (%)
Reactive	Anionic, water soluble	Wool, cotton, silk and nylon	Covalent bonding	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Anthraquinone, formazan, phthalocyanine, azo, oxazine and basic	50–90	10–50
Sulphur	Colloidal, insoluble	Rayon and cotton	Covalent bonding	Aromatic substrate vatted with sodium sulphide and re-oxidised to insoluble Sulphur—containing products on fiber	Indeterminate structures	60–90	10–40
Vat	Colloidal, insoluble	Wool and cotton	Impregnation and oxidation	Water-insoluble dyes solubilized by dropping in sodium hydrogen sulphite, then exhausted on re-oxidised and fiber	Indigoids and anthraquinone	80–95	5–20

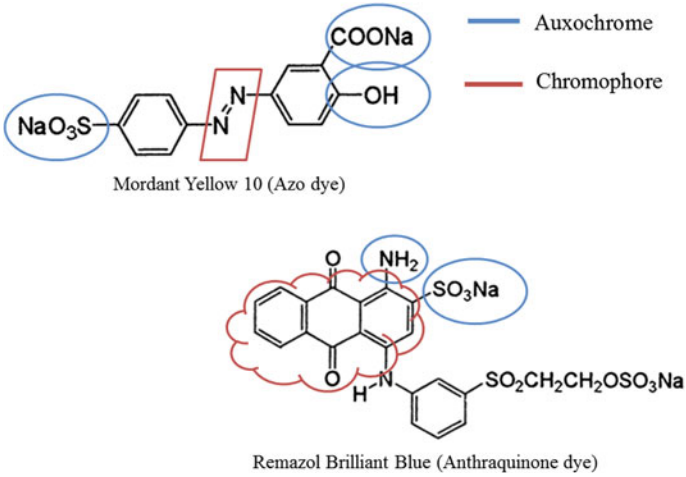
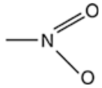
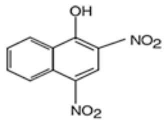
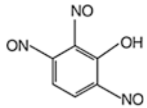
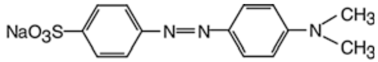
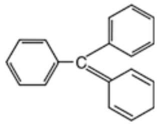
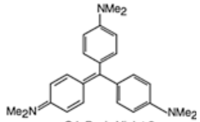
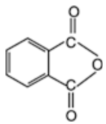
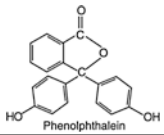


Fig. 2 Examples of dye-auxochromes and–chromophores for azo and anthraquinone dyes. Reprinted with permission of Santos et al. (2007). Copyright © 2016 Elsevier Ltd.

structure such as –C=C–, –C≡N–, –C=O–, –N=N– that are responsible for the dye colors. Functional groups are characterized by the presence of an electron withdrawing or donating substituent (auxochromes cannot undergo π-π* transitions but can undergo transition of n electrons), which enhances the affinity of the dye toward the fibers, consequently enhancing the color intensity. The most common auxochromes are the $–NH_2$, $–NR_2$, –NHR, –COOH, $–SO_3H$, –OH and $–OCH_3$ (Kiernan 2001; Kunz et al. 2002; Colpini et al. 2008; Uday et al. 2016). It is worth mentioning that sulfonate groups confer very high aqueous solubility to dyes (Santos et al. 2007). Table 3 shows the classification of dyes based on the presence of chromophore groups.

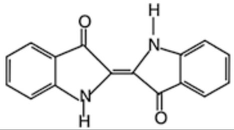
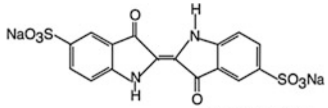
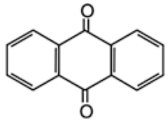
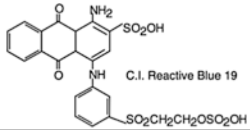
Azo dyes constitute one of the most important groups of synthetic dyes used by textile industries (Holkar et al. 2016; Santos et al. 2016). Among commercial synthetic dyes, azo dyes constitute a group with a broad range of colors and structures and represent up to 70% of the all dyestuffs used worldwide. They are the most common synthetic dyes released into the environment (Saratale et al. 2011; Sen et al. 2016). Azo dyes absorb light in the visible spectrum due to their chemical structure, which is characterized by one or more azo group (–N=N–) bonds to aromatic rings (Fig. 3) (Castanho et al. 2006). The azo group is substituted with benzene or naphthalene groups, which can contain many different substituents, such as chloro (–Cl), methyl ($–CH_3$), nitro ($–NO_2$), amino ($–NH_2$), hydroxyl (–OH), or carboxyl (–COOH), giving different types of azo dyes (Zollinger 1991). The success of azo dyes is due to their simple synthetic procedures, their great structural diversity, their high molar extinction coefficient, and their medium-to-high fastness properties with respect to both light and wetness (Bafana et al. 2011).

Table 3 Classification of dyes based on the chromophore present (Ali 2010)

Class dyes	Chromophore	Example
Nitro		 C.I. Acid Yellow 24
Nitroso	—N=O	 Fast Green O
Azo	—N=N—	 Methyl Orange
Triphenylmethane		 C.I. Basic Violet 3
Phthalein		 Phenolphthalein

(continued)

Table 3 (continued)

Class dyes	Chromophore	Example
Indigo		 C.I. Acid Blue 71
Anthraquinone		 C.I. Reactive Blue 19

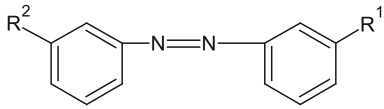


Fig. 3 Basic structure of azo dye. Reprinted with permission of Khan et al. (2013). Copyright © (2012) Springer Science Business Media B.V.

Improper discharge of textile wastewater containing azo dyes and their metabolites into water bodies can cause serious environmental problems, such as visual pollution due to their high coloration, inhibition of photosynthetic processes as result of reduced sunlight penetration, deficiency of dissolved oxygen concentration, changes the life cycle of aquatic organisms and toxicity to aquatic flora and fauna, even at low dye concentrations (Foo and Hameed 2010; Saratale et al. 2011; Simionato et al. 2014; Góes et al. 2016).

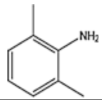
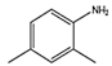
3 Effects of Textile on Environmental and Human Health

Depending on the concentration and exposure time, dyes can have acute and/or chronic effects on exposed organisms (Valh et al. 2011). Today, two classes of dyes, azo and disperse, are recognized worldwide as having the potential to cause allergic contact dermatitis and possibly cancer. They can be cleaved by skin bacteria, or by dermal or systemic metabolism into aromatic amines which might have undesired toxicological properties, particularly due to their carcinogenic or allergenic potential (Platzek 2010; Brüschweiler et al. 2014). After a detailed literature search of 43 high priority substances, Brüschweiler et al. (2014) organized two priorities lists. Priority list A (Table 4) contains 15 (potentially) carcinogenic and/or genotoxic substances; priority list B (Table 5) contains 11 substances that may (potentially) cause sensitization by skin contact.

Textile contact dermatitis (TCD) results from contact between the skin and substances used in clothing. Finishing products (finish resins) and dyes are the main causes of TCD. During contact there can be perspiration, which involves moisture transport between the skin and the dyed and finished clothing items. These sensitizing agents (they can be fibers, dyes, or finish resins) are transported by transpiration into the skin and can cause skin irritation, including eczematous dermatitis (in most cases), urticaria, purpura, erythema multiforme, and erythroderma (Brookstein 2009; Sánchez-Gilo et al. 2010).

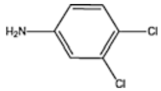
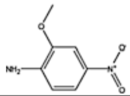
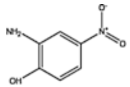
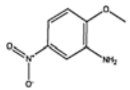
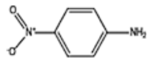
Besides causing contact allergies and dermatitis, if toxic dyes are able to penetrate the skin and enter the body, they can also induce other kinds of harmful effects to the exposed cells. The possible deleterious effects include DNA damage, kidney and pancreatic problems, nervous system damage and even cancer (Leme et al. 2014).

Table 4 Priority list A: (Potentially) carcinogenic and/or genotoxic aromatic amines (Brüschweiler et al. 2014)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound)
2,6-Xylidine 2,6-Dimethylaniline	87-62-7		IARC Carc. Cat. 2B (possible human carcinogen) EU Carc. Cat. 3; R40 (limited evidence of a carcinogenic effect) MAK Carc. Cat. 2 (DFG)	C.I. Acid Orange 134
2,4-Xylidine 2,4-Dimethylaniline	95-68-1		MAK Carc. Cat. 2 (DFG)	C.I. Acid Red 8 C.I. Acid Red 26 C.I. Acid Red 40 C.I. Acid Red 135 C.I. Acid Red 170 C.I. Acid Orange 17 C.I. Direct Red 126 C.I. Direct Red 168 C.I. Solvent Orange 7 C.I. Solvent Yellow 18

(continued)

Table 4 (continued)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound)
3,4-Dichloroaniline	95-76-1		Limited genotoxicity testing produced equivocal results Positive sister chromatid exchange test, evidence of induction of spindle damage, negative micronucleus test). No carcinogenicity study available	C.I. Disperse Yellow 241
2-Methoxy-4-nitroaniline 4-Nitro-o-anisidine	97-52-9		R40 (limited evidence of a carcinogenic effect) Positive in vitro genotoxicity tests (Ames-test, chromosomal aberration). It is on the NTP candidate list for carcinogenicity study	C.I. Disperse Red 41
2-Amino-4-nitrophenol	99-57-0		TD50 = 839 mg/kg bw/day (rat) Inadequate evidence in humans for the carcinogenicity Limited evidence for the carcinogenicity in experimental animals Not classifiable as to its carcinogenicity to humans (IARC group 3)	C.I. Acid Brown 349 C.I. Acid Yellow 119 C.I. Mordant Brown 33
2-Amino-4-nitroanisol 5-Nitro-o-anisidine	99-59-2		TD_{50} = 53.9 mg/kg bw/day (rat) SFo = 0.049 1/(mg/kg bw/day) (US EPA) Positive in genotoxicity tests. Increased incidence of tumours in rats and mice Not classifiable as to its carcinogenicity to humans	C.I. Pigment Red 23
4-Nitroaniline	100-01-6		SFo = 0.02 1/(mg/kg bw/day) (US EPA) Significant increase in hepatic hemangiosarcoma in male mice It recommended to classify it as suspected human carcinogen	C.I. Acid Black 1 C.I. Acid Black 210 C.I. Acid Brown 75 C.I. Acid Brown 106 C.I. Acid Brown 123

(continued)

Table 4 (continued)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound)
				C.I. Acid Brown 348 C.I. Acid Brown 349 C.I. Disperse Orange 1 C.I. Disperse Orange 1.1 C.I. Disperse Orange 3 C.I. Disperse Orange 25 C.I. Disperse Orange 29 C.I. Disperse Orange 31 C.I. Disperse Orange 33 C.I. Disperse Orange 49

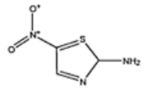
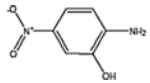
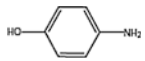
(continued)

Table 4 (continued)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound)
				C.I. Disperse Orange 73 C.I. Disperse Orange 80 C.I. Disperse Red 1 C.I. Disperse Red 2 C.I. Disperse Red 17 C.I. Disperse Red 19 C.I. Disperse Red 74 C.I. Disperse Red 135 C.I. Disperse Red 278 C.I. Mordant Orange 1

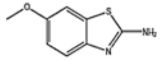
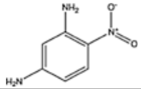
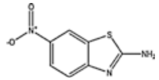
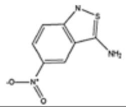
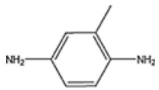
(continued)

Table 4 (continued)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound)
2-Amino-5-nitrothiazol	121-66-4		TD50 = 44.6 mg/kg bw/day (rat) Limited evidence for the carcinogenicity in experimental animals	C.I. Disperse Blue 102 C.I. Disperse Blue 106 C.I. Disperse Blue 124
2-Amino-5-nitrophenol	121-88-0		TD_{50} = 111 mg/kg bw/day (rat) Inadequate evidence in humans for the carcinogenicity Limited evidence in experimental animals for the carcinogenicity Not classifiable as to its carcinogenicity to humans (IARC Group 3)	C.I. Disperse Red 16
4-Aminophenol	123-30-8		EU Muta. Cat. 3; R68 (possible risk of irreversible effects)	C.I. Acid Orange 33 C.I. Disperse Orange 13 C.I. Disperse Orange 29

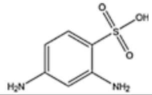
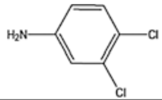
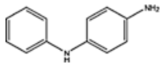
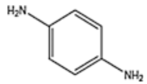
(continued)

Table 4 (continued)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound)
2-Amino-6-methoxybenzothiazol	1747-60-0		Some evidence for genotoxicity	C.I. Disperse Red 379
4-Nitro-1,3-phenylenediamine	5131-58-8		Evidence for genotoxicity (some Ames-tests positive, chromosome aberration positive, sister chromatid exchange weakly positive)	C.I. Acid Brown 83
2-Amino-6-nitrobenzothiazol	6285-57-0		Positive Ames-tests	C.I. Disperse Red 177 C.I. Disperse Red 179
3-Amino-5-nitro-2,1-benzisothiazol	14346-19-1		Positive Ames-tests	C.I. Disperse Blue 148
2,5-Diaminotoluene *p*-Toluenediamine	25376-45-8		Increased tumours in liver, mammary gland and lung of rats EU Carc. Cat. 2; R45 (may cause cancer) EU Muta. Cat. 3; R68 (possible risk of irreversible effects) EU Repr. Cat. 3; R62 (possible risk of impaired fertility)	C.I. Solvent Red 25

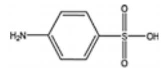
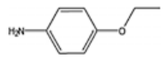
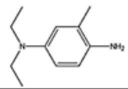
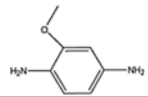
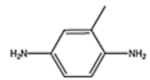
TD50: tumorigenic dose rate 50. SFo: oral slope factor

Table 5 Priority list B: aromatic amines which may cause sensitization by skin contact (Brüschweiler et al. 2014)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound
1,3-Phenylenediamine-4-sulfonic acid	88-63-1		R43 (may cause sensitization by skin contact)	C.I. Acid Brown 123
3,4-Dichloroaniline	95-76-1		R43 (may cause sensitization by skin contact)	C.I. Disperse Yellow 241
N,N-Dimethyl-1,4-Phenylenediamine *N,N*-Dimethyl-*p*-benzenediamine	99-98-9		Contact dermatites (HSDB)	C.I. Basic Blue 54 C.I. Disperse Red 4 C.I. Solvent Yellow 2 Janus Green B
4-Aminodiphenylamine	101-54-2		R43 (may cause sensitization by skin contact) Contact dermatites (HSDB)	C.I. Acid Yellow 36 C.I. Disperse Orange 1
p-Phenylenediamine	106-50-3		R43 (may cause sensitization by skin contact)	C.I. Acid Brown 4 C.I. Acid Brown 237 C.I. Acid Green 11 C.I. Acid Red 151 monolithium salt C.I. Acid Yellow 159 C.I. Direct Black 8 C.I. Direct Black 19 disodium salt C.I. Direct Red 81 C.I. Direct Red 253 C.I. Disperse Black 1 C.I. Disperse Black 2 C.I. Disperse Orange 3

(continued)

Table 5 (continued)

Cleavage product	CASRN	Chemical structure	Points of concern	Azo dye parent compound
Sulfanilic acid 4-Aminobenzene sulfonic Acid	121-57-3		R43 (may cause sensitization by skin contact)	C.I. Acid Black 210 C.I. Acid Brown 106 C.I. Acid Orange 7 C.I. Acid Orange 156 C.I. Acid Red 151 C.I. Direct Brown 44 C.I. Direct Red 80 C.I. Direct Red 81 C.I. Direct Red 253
4-Aminophenol	123-30-8		Known allergen (HSDB)	C.I. Acid Orange 33 C.I. Disperse Orange 13 C.I. Disperse Orange 29
4-Ethoxyaniline *p*-Phenetidine *p*-Aminophenetol	156-43-4		R43 (may cause sensitization by skin contact)	C.I. Acid Yellow 38 C.I. Acid Yellow 159 C.I. Direct Yellow 12
4-(*N,N*-Diethyl)-2-methyl-*p*-phenylenediamine monohydrochloride	2051-79-8		R43 (may cause sensitization by skin contact)	C.I. Acid Red 397 C.I. Disperse Red Dye
1,4-Diamino-2-methoxybenzene	5307-02-8		Contact dermatites is common (HSDB)	C.I. Acid Yellow 219 C.I. Disperse Orange 29
2,5-Diaminotoluene *p*-Toluenediamine	25376-45-8		R43 (may cause sensitization by skin contact) A potent skin sensitizer (HSDB)	C.I. Solvent Red 25

Textile dyes also affect human metabolism through the food chain, causing kidney and respiratory problems, and hypertension, among others. Studies carried out with workers in the textile industry indicated that these professionals are more prone to pancreatic cancer, bladder cancer and cancer of the digestive system because they are exposed to dyes on a daily basis (Peralta-Zamora et al. 2002; Aksu and Donmez 2005; Sanghi and Verma 2013).

Azo and nitro dyes are reduced in the intestinal environment, resulting in the formation of toxic amines in both cases (Chung et al. 1978; Weber and Wolfe 1987). Studies have linked exposure to dyes in textile workers and increased risk of bladder, digestive system and pancreatic cancer (Dolin 1992; Notani et al. 1993; Alguacil et al. 2000; Mastrangelo et al. 2002). Vineis and Pirastu (1997) reported that exposure of workers to aromatic amines increases the incidence of bladder cancer by 25%.

Bosetti et al. (2005) conducted a population-based study in Canada and found a positive association between bladder cancer and occupational exposure to paints in workers in the textile industry. De Roos et al. (2005) also observed an increase in the risk of colon cancer in textile workers exposed to dyes for a long period (20 years or more). Other studies also found an association between esophageal cancer and workers in the textile industry (Wernli et al. 2006).

Wastewaters from the textile industry are usually polluted with recalcitrant or hazardous organics, such as dyes, surfactants, metals, salts, and persistent organic pollutants (POPs) (Valh et al. 2011). These industries discharge large volumes of wastewaters into aquatic environments, which may affect aquatic organisms both directly and indirectly, through the trophic chain or by resuspension, which may make pollutants bioavailable and enable them to reach human beings (Garcia et al. 2012). Verma et al. (2012) summarized the harmful direct and indirect effects of textile wastewaters in the environment as shown in Fig. 4.

Although textile wastewaters are variable mixtures of many pollutants, their major characteristic is high coloration due to the presence of dyes. This high coloration coupled with high organic load induces perturbation to aquatic life and causes dramatic aesthetic pollution (Blanco et al. 2014; Gupta et al. 2015), which cannot be tolerated by local populations (Verma et al. 2012). The greatest environmental concern about dissolved dyes in water bodies is not only their visibility, but also because they absorb sunlight and can hinder light penetration in the water (rivers, lakes, lagoon, etc.) and, hence reduce the photosynthetic activity of aquatic flora. As a result, there is a significant reduction in the oxygenation capacity of the water, disturbing the whole aquatic ecosystem and the food chain (Xu et al. 2005; Merzouk et al. 2010; Valh et al. 2011; Chhabra et al. 2015). Dissolved dyes can also cause an increase in air pollution in terms of stringent foul odors, inorganic carbon deposits, changes of the soil matrix (Senthilkumar et al. 2011) and ground water systems are affected due to leaching through the soil (Khaled et al. 2009).

When dyeing wastewater is disposed of without appropriate, or any, treatment, into water bodies, it can form a thin layer of discharged dyes over the surface and also decrease the amount of dissolved oxygen in the water, thereby affecting the aquatic fauna (Ali 2010) and increasing the BOD of the contaminated water

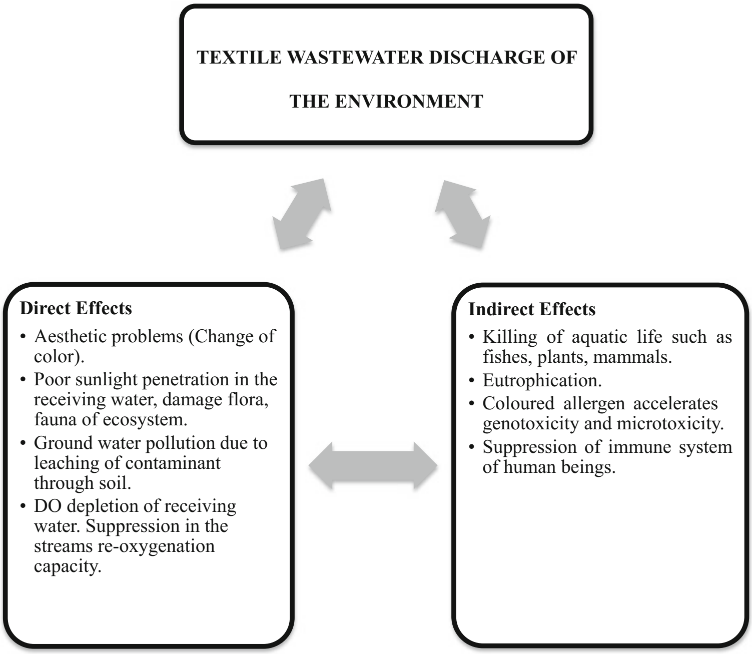


Fig. 4 Effects of textile wastewater into the environment. Reprinted with permission of Verma et al. (2012). Copyright © 2011 Elsevier Ltd.

(Annuar et al. 2009). Apart from this, several dyes and their decomposition derivatives have proved to be toxic to aquatic life such as crustaceans (Bae and Freeman 2007; Ferraz et al. 2013), microorganisms (Gottlieb et al. 2003), fish (Oliveira et al. 2016), and algae (Sponza 2006).

4 Coagulation/Flocculation Process (CF)

Currently, there is an increased interest in the decolorization and decontamination of industrial textile wastewater (Garcia et al. 2009). Different treatment technologies have been studied in order to solve the problems caused by the toxic substances contained in industrial textile wastewater, such as electrocoagulation (Naje et al. 2016; Ozyonar 2015), adsorption (Simionato et al. 2014; Góes et al. 2016), photocatalytic process (Souza et al. 2016, 2017; Garcia et al. 2012; Palácio et al. 2012), ozonation (Castro et al. 2016), membrane bioreactor (Jegatheesan et al. 2016; Deveci et al. 2016) and anaerobic/aerobic biological treatment (Abiri et al. 2016). However, these methods are neither economically nor technologically suitable for large scale use and normally require the combination of two or three methods to achieve an appropriate level of color removal (Robinson et al. 2001; de Souza et al. 2016).

Coagulation/flocculation (CF) is the most widely used technique in industrial wastewater treatment worldwide (de Souza et al. 2016) because it is relatively simple and inexpensive to operate (Fu and Wang 2011). It has been reported that the Egyptians were using aluminum sulfate (alum) to cause suspended particles to settle in water as early as 1500 BC. Although the early Romans were also familiar with alum, it was not until 77 AD that its utilization as a coagulant in water treatment was firs recorded (Teh et al. 2016). Today, the coagulation-flocculation process is a vital step in removal of colloidal particles, natural organic matter, microorganisms and inorganic ions present in untreated water (Eckenfelder 1966; Renault et al. 2009; Kakoi et al. 2016).

The inherent disadvantage to this process is its generation of large quantities of chemical sludge that is classified as hazardous waste that must be disposed of in secure landfills. The process also increases the total dissolved salt content in the treated wastewater, increasing desalination costs by a substantial margin. On the other hand, coagulant aids are inorganic materials that, when used alongside a main coagulant improve or accelerate the process of coagulation and flocculation by producing quick forming, dense and rapidly settling flocs. Coagulant aids increase the density of slow settling flocs and add toughness to the flocs so that they do not break up during the mixing and settling processes (Holt et al. 2002; Sahu and Chaudhari 2013).

The efficiency of CF its operational costs depend on several factors, including the coagulant type and dosage, mixing conditions, pH, temperature, ionic strength, as well as the nature and concentration of the organic matter, the total dissolved solids, the size and distribution of the colloidal particles in suspension among others (Rodrigues et al. 2008; Santo et al. 2012).

4.1 Physical-Chemical Concepts About Coagulation/Flocculation Process

Colloids that contain charged particles remain stable, since the forces of Coulomb repulsion between charges of the same sign are stronger than attractive van der Waals forces. For coagulation to occur it is necessary to destabilize these electric charges. One of the most used models for the explanation of the coagulation phenomenon is the double diffuse layer model.

According to the dual layer model, negatively charged micelles are associated with an electric field around them in the water that contains positively charged (+) cations and negative (−) anions. Immediately, the hydrated cations will be attracted and will be disposed on the negative surface of the micelles to neutralize the electric field, obeying Coulomb's law given by Eq. (1).

$$F = \frac{q^+ q^- (micelle)}{4\Pi\varepsilon_0 r^2} \tag{1}$$

However, as the electric field is neutralized by the positive charges, there remains an electric field “residue”, whose force is counterbalanced by the kinetic energy (temperature dependent) of the ions, and a disorganized (or unstructured) region is formed because the force resulting from the kinetic energy of the particles present on it is greater than or equal to the force of attraction resulting from the electrostatic and van der Waals forces.

The diffuse layer theory has as basic postulates:

I. Interactions are electrostatic;
II. The retention force decreases between the negative charges (−) of the micelle and the adsorbed cations with distance, establishing two defined attraction zones: adsorbed cations—”internal solution”; cations and anions in equilibrium—”external solution”;
III. A balance governed by thermodynamics is established between the two: the increase of a factor in one of the phases implies compensation in the other and vice versa.

There are two double layer diffusion models:

In the Helmhorltz model (originating in mid-1879), the counter ions of the solution move to the vicinity of the charged micelle, forming a layer of ions adhering to the micelle and creating a potential Ψ there. The Helmhorltz model assumes that the decrease in the force of attraction between counterions and micelles, that is, the decrease in potential, is rapid with distance.

According to the diffuse double layer model (Stern Model), there is an adhered layer and, outside of it, a diffuse layer around the colloidal micelle. Therefore, the potential Ψ and the attractive forces between the micelle and the counterions first fall rapidly at first (in the adhered layer), and then slowly in the diffuse layer, as shown in Fig. 5.

Analyzing the two models for the diffuse double layer it can be concluded that there are three potentials that can be estimated:

The Ψo potential on the micelle surface.

The potential Ψ on the inner surface of the double layer where the diffuse layer begins.

The potential ς (zeta) in the shear plane. The shear plane is the section of the double layer that moves along with the colloidal particle. It is located between the inner and outer surfaces of the double layer. Since the particle cannot be separated from its counterions, the only potential that can be determined is the potential ς, and the knowledge of this potential is important in order to achieve destabilization of the colloidal particles.

The resultant interaction between the repulsive Coulomb forces and attractive van der Waals forces creates an energy barrier that prevents the approach of colloidal particles, since the repulsive forces are more intense. This energy barrier

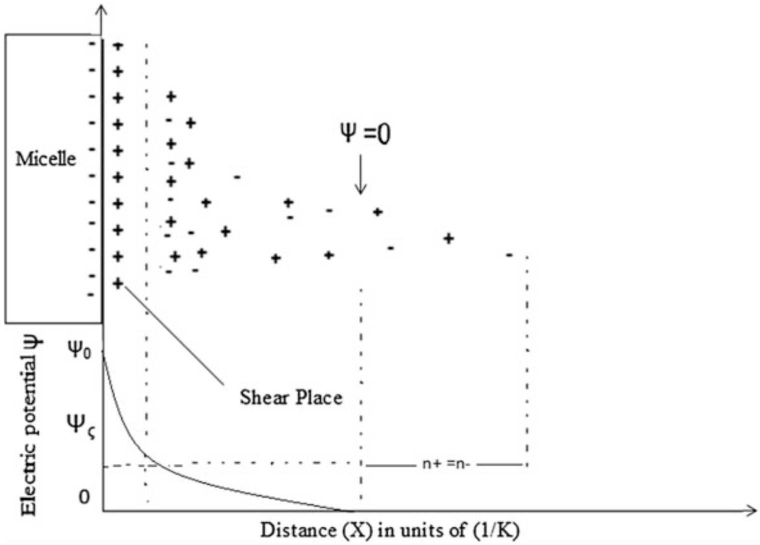


Fig. 5 The double layer model proposed by Stern. Adapted by Lenzi et al. (2009)

varies with pH (pH dependent charge). The distance between micelles at which flocculation can occur, which is achieved when the potential ς is null can be approximated; this point is called the isoelectric point. The isoelectric point can be achieved by neutralizing the micelle charges or by decreasing the thickness of the double electrical layer.

From an electrostatic point of view, coagulation is the reduction of the zeta potential by the addition of specific ions. Coagulation occurs when the addition of a cationic electrolyte decreases the zeta potential, because the electrolyte reduces repulsive forces and allows the action of van der Waals attractive forces to promote agglutination. The required electrolyte dosage depends on the concentration of the colloids (Leme 1982; Lenzi et al. 2009).

In order for efficient coagulation to take place, intense mixing must be achieved by suitable agitation, which has the function of producing turbulence and is characterized by the velocity gradients it creates. An intense mixture ensures uniform distribution of the coagulant into the water by contacting the particles in suspension before the reaction is complete. Flocculation consists of clustering and compaction of the suspended particles in large sets called flakes, which is achieved by limited slow stirring to avoid breaking already formed flakes.

In the mixture, flotation decisively influences the preparation for decanting. It refers to the gathering of coagulated material into larger and denser particles, called flakes (Leme 1979).

4.2 CF Mechanism

The process of coagulation or destabilization of colloidal particles may occur through four types of mechanisms: adsorption and bridging; double-layer compression; charge neutralization; and sweep coagulation. Each of these mechanisms is considered below.

4.2.1 Adsorption and Bridging

Bridging between particles occurs with the introduction of long-chain polymers or polyelectrolytes, as these coagulants are capable of extending into the solution to capture and bind multiple colloids together. The bridging efficiency is further improved when coagulants with larger molecular weights are used, due to their extended polymeric chains. Natural polymers such as polysaccharides and proteins can also induce coagulation via bridging. Such a mechanism has been recognized since the 1950s (Ruehrwein and Ward 1952) and is extremely important in practice. An essential requirement for bridging flocculation is that there should be sufficient unoccupied surface on the particles for attachment of segments of polymer chains adsorbed on other particles. It follows that the adsorbed amount should not be too high, otherwise the particle surfaces will become so highly covered that there are insufficient adsorption sites available (Bolto and Gregory 2007; Choy et al. 2015).

In general, if the molecular weight is high and the charge density is low, the polymer adsorbs on the particle surface in such a way that tails and loops extend far beyond the surface and can interact with other particles (Rasteiro et al. 2008). The consequence of bridging flocculation is that the flocs produced can be much stronger than those formed when particles are destabilized by simple salts (Li et al. 2006).

4.2.2 Double-Layer Compression

This mechanism involves the reduction of the double layer around the colloidal particle by a change in ionic strength induced by the addition of a different electrolyte, which results in the destabilization of colloid (Teh et al. 2016). Under stable conditions in which the concentration of counter-ions is low, colloidal particles are unable to get close to each other because of their thick double electrical layer. However, as the concentration of counter-ions increases via the addition of salts, the diffuse layer becomes thinner and particles can approach more closely before experiencing repulsion. It has been speculated that compression of the electrical double layer is the dominant coagulation mechanism for divalent ions, principally Ca^{2+} and Mg^{2+}, in the normal pH range of water treatments (Duan et al. 2009).

4.2.3 Charge Neutralization

Charge neutralization is the process of adding cationic metals or polymers to neutralize the negative charges of the particles. This coagulation mechanism involves the adsorption of an oppositely charged coagulant on the colloidal surface. It is well known that electrostatic interactions give strong adsorption in these systems and that neutralization of the particle surface and even charge reversal can occur. There is thus the possibility that flocculation could occur simply as a result of the reduced surface charge of the particles and hence a decreased electrical repulsion between them (Bolto and Gregory 2007; Choy et al. 2015; Teh et al. 2016).

4.2.4 Sweep Coagulation

Sweep coagulation is a mechanism related to metal coagulants like Al^{3+} and Fe^{3+}. If a high concentration of these metals is added to water, a large quantity of metal hydroxide will be produced. This amorphous hydroxide will settle, and sweep colloidal particles in its way downward (Renault et al. 2009).

Sweep flocculation generally gives considerably better particle removal than destabilization by charge neutralization alone. At least part of the reason is the greatly improved rate of aggregation, because of the increased solid concentration. Hydroxide precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and, hence, a high probability of capturing other particles (Duan et al. 2009).

5 Chemical Coagulants

The CF process is a complex phenomenon that involves several interrelated parameters, thus it is very important to choose the right coagulant. Chemical coagulants can be categorized into three groups, as shown in Fig. 6 (Verma et al. 2012).

The most common inorganic coagulants are aluminum and iron salts such as $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$, and $Fe_2(SO_4)_3$ due to their low cost, ease of use, handling, storage and mixing properties (Matilainen et al. 2010; Sher et al. 2013). When added to water, aqueous Al (III) and Fe (III) salts dissociate to their respective trivalent ions, i.e. Al^{3+} and Fe^{3+}. After that they are hydrolyzed and form several soluble complexes possessing highly positive charges, thus adsorbing onto the surfaces of negative colloids (Leme 1979; Teh et al. 2016).

Despite the wide applicability of these salts, their use has been questioned due to the iron salts producing brownish coloring of equipment, and environmental impacts caused by high concentrations of residual aluminum in treated wastewater and/or sludge (Matilainen et al. 2010; Zhu et al. 2011; de Souza et al. 2016a). Furthermore, epidemiological, neuropathological and biochemical studies suggest a

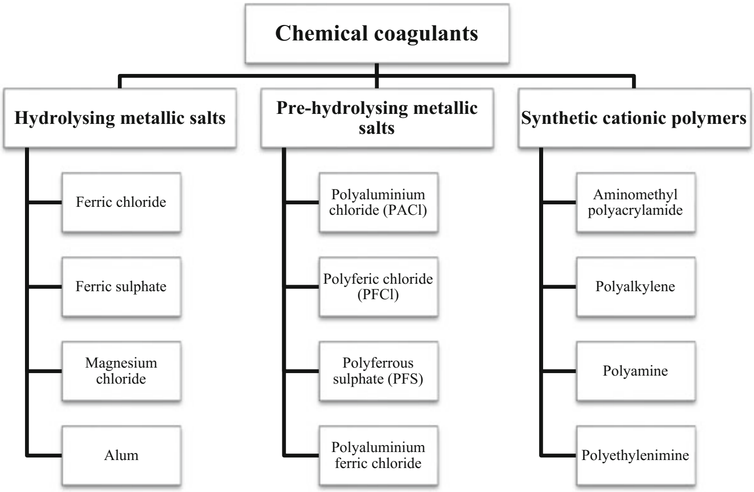


Fig. 6 Schematic category of chemical coagulants by their efficiency. Reprinted with permission of Verma et al. (2012). Copyright © 2011 Elsevier Ltd.

possible link between the neurotoxicity of aluminum and the pathogenesis of Alzheimer's disease (McLachlan 1995; Polizzi et al. 2002; Banks et al. 2006; Walton 2013).

Textile wastewater treatment using inorganic coagulants is not always efficient enough. There are several drawbacks associated with their usage, such as ineffectiveness at low temperatures, harmful effects on human health, the production of large sludge volumes and changes in the pH of the treated water (Choy et al. 2014; Shamsnejati et al. 2015). Under different environmental conditions such as extreme pH and very low or very high temperatures, very sensitive, fragile flocs may be produced, which result in poor sedimentation. These flocs may rupture under any type of physical force (Verma et al. 2012).

To improve the efficiency of the coagulation process, to minimize the hazards of the use of inorganic salts and to obtain wastewater of good quality and fast sedimentation, organic polymers may be recommended (Aguilar et al. 2005; Verma et al. 2012; de Souza et al. 2016a). Organic polymers are water soluble and can be classified into two broad categories: natural and synthetic (Zahrim et al. 2011). Coagulants based on synthetic polymers contain pollutants that may threaten health and the environment. Some of their derivatives are non-biodegradable and the intermediate products of their degradation are hazardous (Oladoja 2015). These pollutants are derived from unreacted monomers (such as acrylamide, diallymethyl ammonium chloride), unreacted chemicals used to produce the synthetic polymers (such as epichlorohydrin, formaldehyde), and reaction by products of the polymers in water (such as *N*-nitrosodimethylamine). The formation of undesirable secondary products may also occur, for example, acrylamide is very much toxic, gives severe neurotoxic effects and has been shown to be carcinogenic, particularly affecting the thyroid, mammary and adrenal glands, the scrotum and the oral cavity (Bratby 2007; Zahrim et al. 2011). Synthetic polyacrylamides are the main organic polymer used in water and waste treatment plants, but in many countries their use has already been stopped on the recommendation of the World Health Organization (WHO 2003; Beltrán-Heredia et al. 2011). Hence, many natural coagulants/flocculants have instead been used for the treatment of textile wastewaters (Teh et al. 2016).

6 Natural Coagulants—Plant-Based Coagulants

In view of the need to overcome the drawbacks of inorganic coagulants and synthetic polymers associated with growing environmental concerns worldwide, there is a need to consider other potential alternatives for textile wastewater treatment in order to minimize environmental damage and improve the wellbeing of human populations. Therefore, researchers have shown significantly more interest in the development of natural polymers as coagulants in recent years (Choy et al. 2014, 2016; de Souza et al. 2014, 2016a; Freitas et al. 2015; Shamsnejati et al. 2015).

The use of natural coagulants for the clarification of water and wastewater has been recorded throughout human history since ancient times and it is still current today (Sanghi et al. 2002). Natural organic polymers have been used for more than 2000 years in India, Africa, and China as effective coagulants and coagulant aids at high water turbidities (Asrafuzzaman et al. 2011).

Natural coagulants can be divided into cationic, anionic or nonionic, and hence are also termed as polyelectrolytes (Yin 2010). Examples of natural cationic polymers are chitosan and cationic starches, while some examples of anionic polymers are sulfated polysaccharides and modified lignin sulfonates. Starch and cellulose derivatives are examples of non-ionic natural polymers (Renault et al. 2009). Particles can aggregate and settle out of solution through four basic mechanisms: double layer compression; sweep flocculation; adsorption and charge neutralization; and adsorption and interparticle bridging. Natural coagulants generally exhibit two types of mechanism: adsorption and charge neutralization; and adsorption and interparticle bridging. Adsorption and charge neutralization can occur when suspended particles in solution sorb to oppositely charged ions, while interparticle bridging occurs when polysaccharide chains of coagulants can attach to multiple particles so that particles are bound to the coagulant and need not contact one another. The existence of adsorption and interparticle bridging between dye molecules and polysaccharides is due to the interaction of π-electron systems of dyes and OH^- groups of polysaccharides (Fig. 7) (Miller et al. 2008; Yin 2010; Verma et al. 2012).

Based on their origin of production, natural coagulants can be divided into three categories; plant, microorganism or animal-based as shown in Fig. 8. However, available sources of plant-based coagulants are much more widespread than

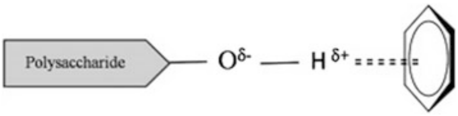


Fig. 7 Schematic representation of intermolecular interaction between π-electron from dye molecule and hydroxyl group of polysaccharide. Reprinted with permission of Verma et al. (2012). Copyright © 2011 Elsevier Ltd.

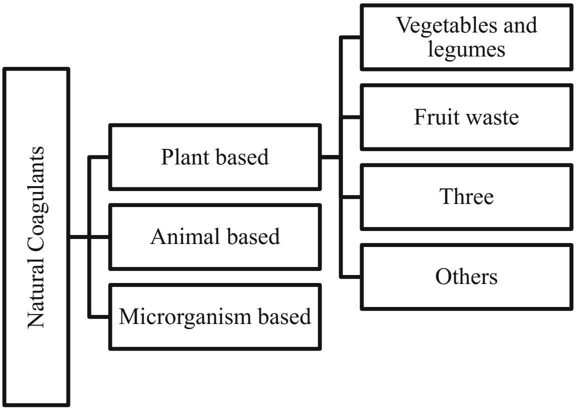


Fig. 8 Schematic categorization of natural coagulants

animal-based coagulants, thus plant-based coagulants could be potential alternatives to chemical coagulants and have gradually gained in importance over the years (Choy et al. 2015).

6.1 Advantage and Disadvantage of Using Plant-Based Coagulants

Organic polymeric compounds have advantages over inorganic materials, as they possess several novel characteristics such as their ability to produce large, dense, compact flocs that are stronger and have good settling characteristics. Natural polymers may potentially be applied not only in food and fermentation processes, and in downstream processing, but also in water and wastewater treatment (Renault et al. 2009) and they can be applied in textile wastewater treatment.

The advantages of using plant-based coagulants in place of inorganic coagulants and/or organic polymers include lower coagulant dose requirements, smaller increases in the ionic load of the treated wastewater, and reduced levels of metals in the treated wastewater (Kakoi et al. 2016). Due to their low toxicological risk (generally free of toxicity) and high biodegradability, they are safe to human health and aquatic life, consequently having a smaller environmental impact (Choy et al. 2016;

de Souza et al. 2016a). One obvious advantage of using renewable materials is their minimal net effect on global warming (Sharma et al. 2006). There are several other advantages: renewable materials generally do not produce secondary pollution (Renault et al. 2009); they usually have a large number of surface charges, which increases the efficiency of the coagulation process; they show environmentally friendly behavior (Freitas et al. 2015); they do not alter the pH of the water under treatment (Oladoja 2015) they are unlikely to produce treated water with extreme pH (Yin 2010); they are also non-corrosive, which eliminates concerns about pipe erosion (Choy et al. 2014).

Plant-based coagulants have been found to generate not only much smaller sludge volumes (up to five times lower) (Ndabigengesere et al. 1995) but also sludge of higher nutritional value (Choy et al. 2014). Wastewaters treated with them pose no risk to biological organisms, in contrast to synthetic coagulants. Furthermore, the sludge produced by natural polymers can be treated by biological processes or disposed of as a soil conditioner due to its non-toxicity (de Souza et al. 2014). As such, sludge treatment and handling costs are lowered, making plant-based coagulants a more sustainable option (Choy et al. 2016).

Using plant-based coagulants can reduce wastewater treatment costs and these advantages are especially augmented if the plants are grown, cropped, and processed locally (Sanghi et al. 2006a; de Souza et al. 2014; Freitas et al. 2015). The raw plant extracts are often available locally and hence, the natural plant-based coagulants are more cost-effective than imported chemicals. Since natural coagulants do not consume alkalinity unlike alum, pH adjustments can be omitted and this provides extra cost savings (Choy et al. 2014; Oladoja 2015).

Plant-based polymeric coagulants are considered "green" because they satisfy the requirements of green technology such as sustainability—meeting the needs of society in ways that can continue into the future without damaging or depleting natural resources; cradle to cradle design—creating products that can be fully reclaimed or re-used; source reduction—reducing waste and pollution by changing patterns of production and consumption; innovation—developing alternatives to technologies that have been demonstrated to damage health and the environment; and viability—creating a center of economic activity around technologies and products that benefit the environment (Oladoja 2015). In the age of climate change, depletion of the earth's natural resources, and widespread environmental degradation, application of these coagulants in textile wastewater technologies is a vital effort and can contribute to advancing global sustainable development initiatives (Miller et al. 2008; Yin 2010). Figure 9 summarizes the benefits of using natural coagulants as an alternative to chemical coagulants.

Plant-based polymeric coagulants also have some disadvantages. Natural polymers are generally non-toxic but synthetic polymers are more effective due to the possibility of controlling their properties such as the number and type of charged units and the molecular weight. Moreover, due to their biodegradability, natural polymers have a shorter storage life than synthetic polymers (Zahrim et al. 2011). Despite the promise shown by these materials, their application has not yet made

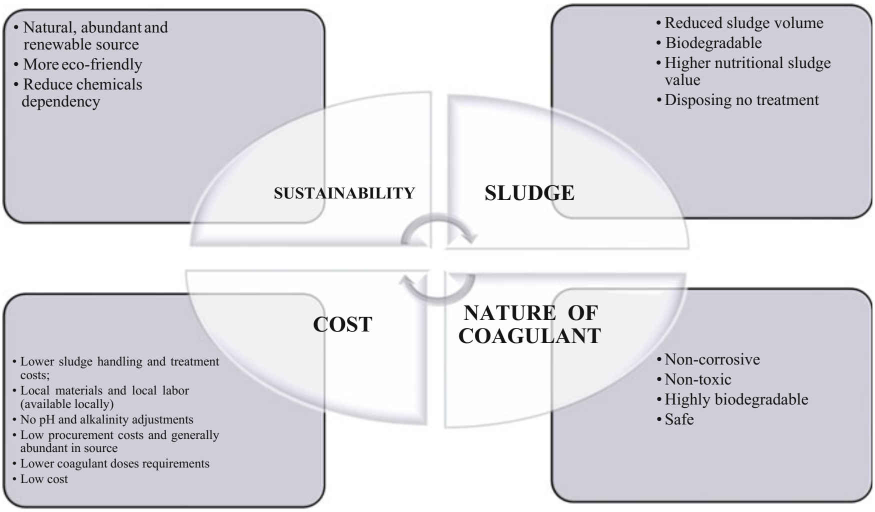


Fig. 9 Advantages of natural coagulants over chemical coagulants. Reprinted with modifications and permission of Choy et al. (2014). Copyright © 2014. Published by Elsevier B.V.

the transition from bench scale to field trials and application in industrial treatment plants (Oladoja 2015).

One of the problems in the use of plant-based coagulants is the substantial increase in the organic load of the treated water, which may result in undesired and increased microbial activities, having serious implications on subsequent disinfection processes using chlorine. Organic matter is regarded as the source of odor, color, and taste (Choy et al. 2014; Oladoja 2015). These organic matters might act a precursor of trihalomethanes (THMs), of which many are carcinogenic and also require chlorine treatment (Anastasakis et al. 2009).

7 Plant-Based Coagulants on Textile Wastewater Treatment

In recent years, natural coagulants extracted from plants have been successfully used in textile wastewater treatment and the number of publications in this area has been growing significantly. This is due to advantages such as biodegradability, safety to human health, low cost, low toxicity and eco-friendliness and abundance. Table 6 summarizes the use of plant-based coagulants in textile wastewater treatment.

Table 6 Research summaries of textile wastewater treatment by coagulation/flocculation process using plant-based coagulants

Coagulant	Sample	Efficiency of coagulation/flocculation process			References
		Turbidity removal (%)	COD removal (%)	Color removal (%)	
Acanthocereus tetragonus	Congo Red			96.7	Chethana et al. (2015)
Alginate from *Sargassum* sp. (Brown Algae)	Sulphur Black Dye			98.2	Vijayaraghavan and Shanthakumar (2015)
Anacardium occidentale	Congo Red Methyl Orange				Edilson et al. (2016)
Azadirachta indica *Cicer arietinum* *Acanthocereus tetragonus* *Moringa oleífera*	Congo Red			95 (Ai) 89 (Ca) 97 (At) 99 (Mo)	Chethana et al. (2016)
Cactus *Cereus peruvianus*	RTW (DF)	85.4	58.3		De Souza et al. (2016a)
Cactus *Opuntia ficus-indica*	RTW (LJ And DF)	91.3 (LJ) 93.7 (DF)	64.5 (LJ) 87.3 (DF)		De Souza et al. (2014)
Cactus *Opuntia ficus-indica*	Painting wastewater	82.6	78.2	88.4	Vishali and Karthikeyan (2015)
Cassia angustifolia seed	Mixture Dyes: Acid Sendula Red Direct Kahi Green Reactive Remazol Brilliant Violet			84 (ASR), 83 (DKG) and 31 (RRBV)	Sanghi et al. (2002)
Cassia fistula Linn seed	Reactive Blue 19 Reactive Black 5			62.0 (RB19) 55.7 (RB5)	Perng and Bui (2015)
Cassia fistula seed	Reactive Red 195			57.8	Manh et al. (2015)
Cassia fistula seed	RTW (DF and DFI)			37.5 (DF) and 71.3 (DFI)	Hanif et al. (2008)

(continued)

Table 6 (continued)

Coagulant	Sample	Efficiency of coagulation/flocculation process			References
		Turbidity removal (%)	COD removal (%)	Color removal (%)	
Cassia javahikai seed	Direct Bordeaux BW Direct Orange Acid Sandolan Red Reactive Procion Brilliant Blue RS RTW			58 (DB), 63 (DO), 5 (ASR), 8 (RPBB) and 25 (RTW)	Sanghi et al. (2006b)
Descurainia sophia L.	Neutral Red Dye			90.2	Ahmadi et al. (2016)
Enteromorpha	Reactive Blue 14 Dye			85–88	Zhao et al. (2014)
Furcraea sp.	Textile industry wastewater	93	80	89	Lozano-Rivas et al. (2016)
Grape (*Vitis vinífera) seed*	Malachite Green Crystal Violet			60 (MG) and 80 (CV)	Jeon et al. (2009)
Moringa oleifera Phaseolus vulgaris	Congo Red			83 73	Vijayaraghavan and Shanthakumar (2015)
Moringa oleifera seed	Direct Black 19 Dye			94.2	Tie et al. (2015)
Moringa oleifera seed	Alizarin Violet 3R			95	Beltrán-Heredia et al. (2009a)
Moringa oleifera seed	Chicago Sky Blue 6b			99	Beltrán-Heredia and Martín (2008)
Moringa oleifera seed	RTW	92.3	92.0	98.8	Hemapriya et al. (2015)
Moringa oleifera seed	Carmine Indigo			80	Beltrán-Heredia et al. (2009b)
Moringa oleifera seed	Reactive Yellow		62	90	Veeramalini et al. (2012)
Ocimum basilicum seed	Congo Red RTW (DF)		61.6 (Dye) 80.4 (RTW)	68.5 (Dye) 76.4 (RTW)	Shamsnejati et al. (2015)

(continued)

Table 6 (continued)

Coagulant	Sample	Efficiency of coagulation/flocculation process			References
		Turbidity removal (%)	COD removal (%)	Color removal (%)	
Okra waste (*A. esculentus*)	RTW (JL)	97.2	85.7	93.6	Freitas et al. (2015)
Plantago major L.	Neutral Red		81.6	92.4	Chaibakhsh et al. (2014)
Plantago ovata seed	RTW (TFI)		89.6		Ramavandi and Farjadfard (2014)
Plantago psyllium	Golden Yellow Dye Reactive Black 5			71.4 (GY) 35 (RB5)	Mishra and Bajpai (2005)
Plantago psyllium	RTW	90 (SS)			Mishra et al. (2002)
Portunus sanguinolentus	Paint effluent	66.85	59	92.29	Vishali et al. (2016)
Surjana seed powder and *Maize* seed powder	Congo Red dye			98.0 (SSP) and 89.4 (MSP)	Patel and Vashi (2012)
Tamarindus indica	Golden Yellow Direct Fast Scarlet			60 (GY) 25 (DFS)	Mishra and Bajpai (2006)
Vegetal tannin (Polysep3000)	RTW		40–50	96	Aboulhassan et al. (2005)
Vegetal tannin (Tanfloc®)	RTW (JL)	92,1	49.2	76.1	De Souza et al. (2016b)

ASR: Acid Sendula Red Dye; Ai: *Azadirachta indica*; At: *Acanthocereus tetragonus*; Ca: *Cicer arietinum*; COD: chemical oxygen demand; CV: Crystal Violet Dye; DF: dyeing fabric; DB: Direct Bordeaux BW Dye; DFS: Direct Fast Scarlet Dye; DKG: Direct Kahi Green Dye; DO: Direct Orange Dye; GY: Golden Yellow Dye; LJ: laundry jeans fabric; Mo: *Moringa oleífera*; MSP Maize seed powder; MG: Malachite Green Dye; RB5: Reactive Black 5 Dye; RB19; Reactive Blue 19 Dye; RPBB: Reactive Procion Brilliant Blue RS; RRBV: Reactive Remazol Brilliant Violet Dye; RTW: real textile wastewater; SS: suspended solids; SSP: Surjana seed powder; TFI: textile finishing industry

7.1 Tannin

Tannin is a general name given to large polyphenol compounds, it is water-soluble polyphenolic anionic polyelectrolyte; with a molecular weight around 500 thousand. They are obtained from natural materials, for example, the organic extract from bark and wood of trees such as Acacia, Castanea, or Schinopsis (Yin 2010).

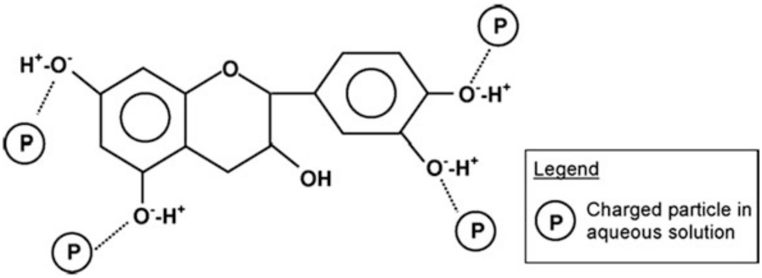


Fig. 10 Schematic representation of basic tannin structure in aqueous solution and possible molecular interactions. Reprinted with permission of Yin (2010). Copyright © 2010 Elsevier Ltd.

They also is found in some plants, such as in the seeds of *Cassia obtusifolia* (Subramonian et al. 2014) and *Castanea sativa* trees (Chestnut) (Oladoja 2016). The chemical structure is complex and cannot be accurately determined, but it is known that carboxyl and hydroxyl groups predominate. Studies have shown the efficiency of tannin as a coagulant and flocculant (Choy et al. 2014; Oladoja 2016). Widely known and studied, tannin may be used as coagulant in the treatment of textile wastewater, and can be modified for use as a cationic polyelectrolyte to remove anionic compounds (Beltrán-Heredia et al. 2011).

Figure 10 illustrates the schematic representation of basic tannin structure in aqueous solution and possible molecular interactions that induce coagulation. It is common knowledge that phenolic groups can easily deprotonate to form phenoxide which is stabilized via resonance. This deprotonation is attributed to delocalization of electrons within the aromatic ring which increases the electron density of the oxygen atom (Yin 2010).

7.2 *Moringa oleifera*

Moringa oleifera is a tropical plant found in Asia, India, Africa and Latin America, is reported that its seeds are used to clean turbid river water in rural communities in African countries. It is the most studied natural coagulant in environmental science. Its coagulant potential can be improved by the addition of bivalent cations as Ca^{2+} and Mg^{2+} (Yin 2010). It also can be used to improve the efficiency of other natural coagulants.

Kansal and Kumari (2014) reported the coagulant efficacy of *Moringa oleifera* on seven pigments, with a removal of 60–99%. When applied as coagulant in Congo Red pigment solution, a concentration of only 25 mg/L of *M. oleifera* seeds solution removed 98% of the pigment. The seed also showed satisfactory removal of turbidity caused by the pigment Black 19, demonstrating that this species is one of the most promising natural coagulant species for textile wastewaters (Tie et al. 2015).

7.3 *Ocimum basilicum*

Ocimum basilicum is popularly known as basil, and can be found in tropical regions in Asia, Africa, Central America and South America. It has many different applications, from use as a condiment to applications in traditional medicine. Its seeds have been used in CF processes and have shown good results. When soaked in water, the seeds create mucilage rich in pectin. The seed extract is rich in polysaccharides, glucomannan and $1 \rightarrow 4$ bounded xylan, with a small proportion of glucan. After polysaccharide extraction in water, a viscous solution was obtained, which was used as coagulant to treat textile wastewater and Congo red pigment solution. Using only 1.6 mg/L of coagulant, it was possible to remove 61.6% of the COD and 68.5% of the color from a 50 mg/L solution of pigment. When used on real textile wastewater, the removal was of 50.9% and 56.6% for color and COD, respectively, using 9.6 mg/L of *Ocimum basilicum* coagulant solution (Shamsnejati et al. 2015; Oladoja 2015).

7.4 *Cereus peruvianus*

There are many studies with different cactus species describing their use as coagulants and flocculants (Zhang et al. 2006; Miller et al. 2008). De Souza et al. (2016) reported the efficiency of *Cereus peruvianus* for the treatment of textile wastewater. Mucilage extracts were applied to tests of CF. ANOVA analysis was performed to measure the importance of some significant factors (pH, mucilage and inorganic coagulant). The data were shown to fit a quadratic model and the mucilage concentration was significant for the removal of turbidity and COD. The best conditions were: inorganic coagulant 320.0 mg/L, mucilage 10.0 mg/L and pH 5.0. Removal of turbidity and COD of 85.4% $\pm$ 0.5 and 58.3 $\pm$ 0.2, respectively, were achieved.

7.5 *Galacturonic Acid*

Studies performed with different plant species have reported the presence of galacturonic acid, and attributed efficiency in the CF process to its presence. Freitas et al. (2015) reported the presence of galacturonic acid in okra (*A. esculentus*) where it is probably present in the polymer form, polygalacturonic acid, allowing it to provide a "bridge" to adsorb particles by van der Waals and Coulomb interactions. Figure 11 shows how polygalacturonic acid can interact in the CF process.

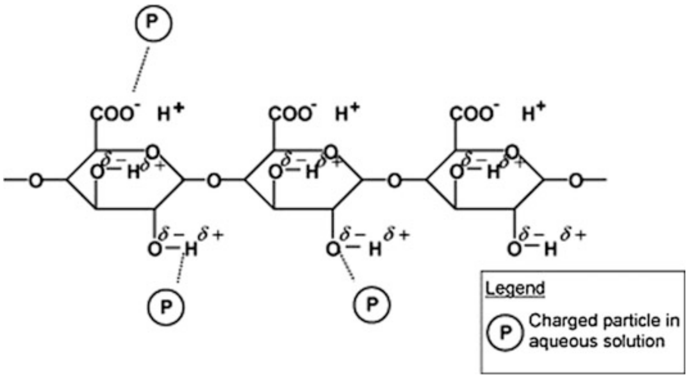


Fig. 11 Schematic representation of polygalacturonic acid in aqueous solution and possible dominant molecular interactions associated with adsorption and bridging. Reprinted with permission of Yin (2010). Copyright © 2010 Elsevier Ltd.

7.6 Cassia *Seed Gums Based Coagulants/Flocculants*

Cassia plants are a known source of seed gums which are usually galactomannans that have close structural resemblance to many commercial seed gums, such as guar and locust bean gums. They are considered as non-conventional renewable reservoirs for galactomannan seed gums. Thus, the properties of Cassia seed gums in general can be tailored by chemical modification whereupon they can be exploited as useful dye flocculants and heavy metal adsorbents depending upon their solubility in water. Though galactomannans from Cassia seeds are nonionic polysaccharides, their adsorption performance is comparable to that of chitin and chitosan, and superior to other polysaccharides (Kalia and Averous 2011).

7.6.1 Cassia Javahikai

Sanghi et al. (2006b) used a *Cassia javahikai* seed gum as a coagulant for the decolorization of textile dye solutions, in combination with very low doses of polyaluminium chloride (PAC). Graft copolymerization with acrylamide was performed to favorably modify the properties of the seed gum. *C. javahikai* (CJ) seed gum, and its copolymer grafted with acrylamide were synthesized in the presence of oxygen using a potassium persulfate/ascorbic acid redox system. Seed gum CJ and its grafted polymer *C. javahikai* (CJG) proved to be very efficient coagulants for the decolorization of direct dyes. In combination with PAC, CJ and CJG were found to be efficient coagulant aids for acids as well as for Procion dyes. The performance of CJG over CJ was more enhanced for direct dyes. Being biodegradable and safe to human health, they can be potential alternatives to conventionally used chemical coagulants.

7.6.2 Cassia angustifolia

Sanghi et al. (2002) evaluated naturally occurring *Cassia angustifolia* (CA) seed gum against the chemical coagulant polyaluminium chloride (PAC) for its ability to remove color from synthetic dye solutions. Three groups of dyes: Acid Sendula Red, Direct Kahi Green and Reactive Remazol Brilliant Violet were chosen for the case study. CA was found to be a good working substitute alone or in conjunction with a very low dose of PAC for decolorization of acid and for direct, but not reactive, dye solutions. It may be concluded that Cassia seed gum can be an effective coagulant aid for direct and acid dyes. It can act as a working substitute, partially or fully, for synthetic chemical coagulants such as PAC.

7.6.3 Cassia fistula

Hanif et al. (2008) carried out textile wastewater treatment using a *Cassia fistula*-based natural coagulant. The dosage of *C. fistula* used in the study was in the range 250–1500 mg L^{-1}. The reduction of TDS was of 86.02–88.39%, and the COD presented a reduction of 37.45% at a dosage of 1500 mg L^{-1}. The efficiency of treatment of textile industry wastewater was found to be dependent on the dosage of the coagulant as well as on the pH of the wastewater.

Perng and Bui (2015) developed a study in order find a new environmentally friendly coagulants that could partially replace conventional polyaluminum chloride (PAC), which has been shown to be toxic to aquatic environments. Gum extracted from the seeds of Cassia *fistula* Linn. (CF) was investigated for the decolorization of the reactive dyes Blue 19 (RB19) and Black 5 (RB5), using jar-test experiments. The decolorization of these dyes by CF gum was highly dependent on pH, probably because it affects the structure of the dyes, the gum and their interactions. The best results were obtained at pH 10. When the gum alone was used for RB19 and RB5 removal, the best treatment efficiencies achieved were 62.0% and 55.7%, respectively. However, a combination of low dosages of gum (80 and 120 mg L^{-1}) and PAC (132 mg L^{-1}) showed rather high removal efficiencies of greater than 92%. The amount of PAC coagulant used was reduced by about 40%. These results indicated the potential of using CF gum as a "green" coagulant or for color removal in textile wastewater.

Manh et al. (2015) studied the ability of *Cassia fistula* seed gum to remove the color from Reactive Red 195 solutions in Jar-test experiments. This low-cost coagulant showed great potential for decolorization of Reactive Red 195 dye solution. The best color removal performance obtained was 57.8%, using 200 mg/L of gum, an agitation speed of 45 rpm, IDC at 10 mg/L and 60 min of treatment at pH 10. Decolorization of Reactive Red 195 dye solutions by coagulation with the gum was highly dependent on the pH and coagulant dosage.

7.6.4 Cassia obtusifolia

Subramonian et al. (2014) investigated the potential use of natural *Cassia obtusifolia* seed gum in the treatment of raw and undiluted PPME through coagulation. The recommended conditions (initial pH 5, dosage of 0.75 g/L, 10 rpm and 10 min slow mixing, with 1 min settling time) allowed removal of total suspended solids and chemical oxygen demand of up to 86.9 and 36.2%, respectively. The findings from the present study showed that the coagulation efficiency using *C. obtusifolia* gum was comparable to that of alum. Characterization of the process showed that *C. obtusifolia* gum, alum and their flocs all possessed distinctive features. The study demonstrated that *C. obtusifolia* gum is a promising and effective natural coagulant that can substitute for harmful inorganic coagulants such as alum in the treatment of industrial effluents.

7.6.5 Cassia tora

Sharma et al. (2006) carried out a chemical modification of *Cassia tora* and guar gum through different substitution and grafting reactions. The modified products were tested against kaolin under laboratory conditions vis-a-vis a polyacrylamide-based synthetic flocculant. The tests were performed with the following modified gums: CB-CTG-carbamoylethyl *C. tora* gum; CE-CTG-cyanoethyl *C. tora* gum; CM-CTG-carboxymethyl *C. tora* gum; Q-CTG-quaternized *C. tora* gum; CTG-g-AA-acrylamide-grafted *C. tora* gum; CTG-g-A-acrylonitrile-grafted *C. tora* gum; CB-GG-carbamoylethyl guar gum; GG-g-MMA-methyl methacrylate-grafted guar gum.

The flocculation efficiency of all the chemically modified products was studied. In the case of products synthesized by substitution reactions the flocculation was greatest with Q-CTG (99.65%) due to its effective charge neutralization as well as bridging, attributed to the cationic functional groups (quaternary ammonium groups) introduced into the backbone. In the case of CB-CTG and CB-GG, the settling of particles was 99.05% and 99.0%, respectively attributed to the carbamoyl-ethyl groups introduced into the biopolymer. Settling of particles was 98.58% with CE-CTG due to the introduced cyanoethyl groups. The settling of particles was 97.80% for CM-CTG because it has a large hydrodynamic volume compared with the other substituted products, due to the presence of more hydrophilic carboxymethyl groups in its backbone.

It can be concluded that the flocculation efficiency of most of the chemically modified products of *C. tora* and guar gum is better than that of synthetic flocculants. These modified products can be further exploited for the treatment of many industrial effluents.

7.6.6 Galactomannans of Plants of the Genus *Cassia*

Galactomannan is a polysaccharide and it is present in most legumes. They constitute the second largest group of polysaccharide reservoirs in the plant world, and can be found in several mucilaginous plants. They are commonly found in the seed endosperm of legumes (Reid 1985; Scherbukhin and Anulov 1999). This class is artificially defined as containing more than 90% mannose, forming a β-(1 → 4) linear chain without ramification. They may or may not be branched with galactose with α-(1 → 6) bonds (Reid and Edwards 1995).

They are present in 13 vegetable families: *Annonaceae, Compositae, Convolvulaceae, Ebenaceae, Mimosaceae, Caesalpinaceae, Fabaceae, Lagoniaceae, Malvaceae, Palmae, Solanaceae, Tiliaceae, Umbelliferae and Cuscutaceae* (Scherbukhin and Anulov 1999). The genus *Cassia* (*Fabaceae*) is constituted by more than 600 species including bushes, trees and herbs. It is distributed in tropical

Table 7 Some species of genus *Cassia* and their proportion mannose/galactose (Man/Gal)

Species	Man/Gal	Reference
Cassia absus L.	3.0	Kapoor and Mukherjee (1969), (1971), (1972)
Cassia alata L.	3.3	Sen et al. (1987)
*Cassia angustifolia*Vahl	2.9	Chaubey and Kapoor (2001)
Cassia didymobotrya Fresen.	0.5	Morimoto et al. (1962)
*Cassia fastuosa*Willd. ex Vogel	4.0	Tavares (1994), Mercê et al. (1998)
Cassia fistula L.	3.0	Kapoor and Farooqui (1993), Morimoto and Unrau (1962)
Cassia grandis L. f.	0.7	Bose and Srivastava (1978), Buckeridge et al. (1995)
Cassia javanica L.	3.23	Azero and Andrade (2002)
Cassia leptocarpa Benth	3.0	Anderson (1949)
Cassia marginata Sessé & Moc.	2.7	Tookey et al. (1962)
Cassia nodosa Buch.-Ham. ex Roxb.	3.5	Heidelberger (1955), Rizvi et al. (1971), Kapoor et al. (1994)
Cassia occidentalis L.	3.0	Gupta and Mukherjee (1973, 1975)
Cassia pulcherrima Dehnh.	3.0	Morimoto and Unrau (1962), Unrau and Choy (1970)
Cassia saltiana Steud.	3.2	Morimoto et al. (1962)
Cassia siamea Lam.	2.5	Kapoor et al. (1996)
Cassia sophera L.	1.0	Hakomori (1964)
Cassia spectabilis DC	2.65	Kapoor et al. (1998)
Cassia tora L.	3.0	Srivastava and Kapoor (2005)
Cassia verrucosa Vogel	4.0	Gupta and Gupta (1988)

regions and subtropical regions around the world (Agarkar and Jadge 1999). Commercial exploitation sources of galactomannans have been identified in some species, whose seeds are of medium size and contain more than 40% endosperm (Srivastava and Kapoor 2005).

Different species differ in the proportion of D-mannose and D-galactose, as well as in the levels of galactomannans in their seeds. The ratio of mannose/galactose is one of the main biochemical characteristics of galactomannans; variations in the monomers provide different physico-chemical properties to their structure (Soni and Bose1985; Buckeridge et al. 1995; Ganter and Reicher 1999).

Galactomannans gums differ from each other according to their different Man/Gal ratios (Table 7). The different chemical properties of these gums make them versatile materials used for many different applications, such as their use as natural coagulants.

8 Limitations, Challenges and Perspective in the Use the Plant-Based Natural Coagulants

Over the years, the minimizing environmental impacts and environmental concern are becoming increasingly important, leading to changes in the energy, water and waste management systems by the development of cleaner production and more efficient, reducing of raw-material consumption and pollution prevention (Nouri et al. 2012; Wu et al. 2010). Plant-based natural coagulants show potential as alternative the usage of chemical coagulants in textile wastewater treatment (Choy et al. 2015). Many studies were mentioned in this Chapter highlighting efficiency plant-based coagulants for coagulation/flocculation process, however, all have some limitations and need to be further studied to identification of fine-tuning and process improvements.

It has been espoused in previous sections that usage of plant-based natural coagulants provides environmental benefits and numerous laboratory-scale have proven that they are technically feasible for small-scale utilization (Yin 2010). But the applications have not been able to transit from laboratory scale to field trials and real industrial applications (Oladoja 2015). CF effectiveness and cost depend on coagulant type and dosage, pH, temperature, ionic strength, total dissolved solids, nature and concentration of organic matter in wastewater, as well as both size and distribution of colloidal particles in suspension and several other factors (Rodrigues et al. 2008; Santo et al. 2012). Therefore, optimization of physical-chemical parameters before large-scale implementation is very important. It takes considerable time and work due to physical-chemical characteristics of real textile wastewater may be subject to periodical variation.

The plant growing and planting at large-scale to supply industrial needs is the main challenge for implementing plant-based natural coagulant at the sustainable industry. This fact will provide an immediate increased in industrial costs due to any necessary technical adaptation, the development of new tools and machines and new professionals needs. But in the long term there will be a significate reduction in the process costs, in the pollutants generated by the process as well it can contribute to employment creation provided by cultivation of those plants.

Another related problem with large-scale is in terms of commercialization. The bottom line is that it will always be based primarily on whether the scale-up system can sustain similar treatment performance at comparable (or reduced) cost with the natural coagulants when compared with established chemical coagulants. The direct comparisons in terms of coagulant types, processing stages and prices in different geographical regions are a very complicated task given the different exchange rates, inflation factor and varying accuracies of the costing values (Yin 2010).

In addition, the response and needs of the market will affect the outlook and demands of natural coagulants as a probable replacement of chemical coagulants. While the commercialization of natural coagulants will not be an overnight success, these small steps taken would progressively bridge the gaps and limitations encountered. Figure 12 summarizes these factors which must be taken into considerations for successful commercialization of natural coagulants. Despite the problems faced in commercialization, many natural coagulants have been used in the water and wastewater treatment industries, especially the tannin extracts from the barks of *Acacia mearnsii* tree have been successfully commercialized as Floccotan®, Tanfloc®, Ecotan® and others (Choy et al. 2014).

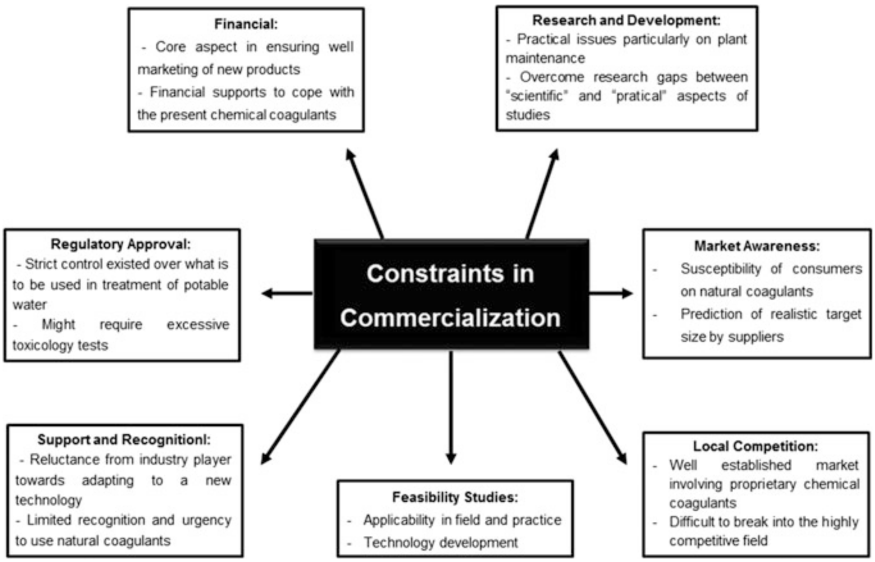


Fig. 12 Factors hindering the commercialization of natural coagulants. Reprinted with permission of Choy et al. (2014). Copyright © 2014 Published by Elsevier B.V.

An evaluation on the economic, social and environmental aspects can be used as a sustainability indicator can be useful with the aid of a pilot plant study. Approval from the local governing bodies should be easily granted for successful commercialization of any new products but they hamper an approval with documentations (Sutherland et al. 2001). Tax rebate, subsidy schemes, tax reduction, incentives environmental laws and regulation should be created by competent bodies to encourage to maximum use of plant-based natural coagulants to resolve the problem.

The dissemination of research findings to the appropriate governmental and non-governmental agencies, who served as an interface between the end users and the researchers, is also lacking. Improvement on this channel of information dissemination can be of great assistance in the implementation of the natural coagulants for real life applications and it also can contribute to resolving the identified problems above (Oladoja 2015).

Understanding the nature of wastewater is fundamental to design suitable wastewater treatment process, to adopt a suitable procedure, determination of acceptable criteria for the residues, determination of a degree of evaluation required to validate the procedure and decision on the residues to be tested based on toxicity (Sahu and Chaudhari 2013). It is required to conduct more and more future research to come up with best natural coagulant or combinations of chemical and natural coagulants. Effectiveness of natural coagulants also required to be carried out against simulated as well as real industrial textile wastewater (Verma et al. 2012). Many studies about simulated wastewater are find in consulted literature but with real wastewater is harder to find.

Despite the sustainable nature of these coagulants, in most cases that the active compound is not isolated and the use of raw extracts has been related, the performance efficiency is low, thus requiring a high dosage of them. Consequent upon the required high optimum dosage, the treated wastewater may contain high levels of residual organic matter; measuring in terms of total organic carbon (TOC) and COD (Oladoja 2016). The substantial increase in the organic load of the treated wastewater is undesirable. It may result to growth in the microbial activities leading the appearance of color, unpleasant odor and producing disagreeable taste (Oladoja 2015).

Conclusive studies about CF mechanism involving natural coagulants are limited and need more research or studies to be understood clearly unlike the widely developed chemical coagulants. The aggregation of colloidal particles may be a result of one or more mechanisms. The procedures for determination and isolation of the active coagulating compounds are too difficult owing to complexity of the process and probable synergistic effects among the components present. Often at times, the active agents responsible for coagulations are made up of different chemical constituents (Choy et al. 2014; Oladoja 2015).

In order to ameliorate the challenges mentioned above, the development of the studies about the CF mechanism can solve them. Thus understanding of the mechanisms of natural coagulants in the CF improves the performance this technique. The characteristics and properties of the flocs formed could reveal important evidence to CF possible mechanisms (Choy et al. 2015). Li et al. (2006) showed that fundamentally different characteristics of flocs such as strength, structure and compactness are essential in establishing the CF mechanisms and the determination of the floc to resistant to breakage is needed to application in industrial scale.

Another factor to be considered to achieve better results in terms CF using natural coagulants is the research of active compound present into plant-based natural coagulant. The extraction, purification, isolation and characterization of the active compound are extremely important to identify the compounds leading to CF. Direct extraction of these compounds could enhance the effectiveness of the overall CF owing to increased relative concentration of the agents. In fact, the coagulant dosage required to achieve optimum coagulation was also significantly reduced by 5–10 times when Marobhe et al. (2007) purified the protein of *V. unguiculata*. This purification also resolves the any problem relating to the presence of the inorganic and organic non-active compounds, which generate an organic load increases (Choy et al. 2014, 2015). For application at large-scale, the plant-based coagulants must be selected according to annual availability of species.

9 Conclusion

The knowledge and scientific research in pollutants removal of wastewater are of utmost importance in order to respond to environmental needs. To meet the increased more and more stringent environmental laws, many different technologies of wastewater treatment have been developed for removal of suspended and dissolved organic matter from textile wastewater. It is evident from a review of current literature that coagulation/flocculation process has been widely used to remove organic matter and color from textile wastewater. The usage of natural coagulants derived from plant-based sources as an alternative to usage of chemical coagulants represents a great development in sustainable environmental technology since it focuses on the improvement of quality of environmental and human health without losing industrial process efficiency. Nonetheless, there are issues that hamper process development of them, such as absence of mass plantation of the plants that affords bulk processing, perceived low-volume market, inexistence of incentive laws and the application is currently restricted to small-scale. In technical terms, these natural coagulants are highly efficient for reduction of physical-chemical parameters of the wastewater such as color, turbidity, COD, TOC, BOD, TSS and others. Planted-based coagulants also have several reasons to become effective coagulant; high cationic charge density, long polymer chains, bridging of aggregates and precipitation, safe, eco-friendly, non-toxic, non-corrosive, high biodegradability, reducing sludge volume, increasing floc size, allowing the reduction of production costs since using raw material from renewable resources.

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