

Review

The Application of Modified Natural Polymers in Toxicant Dye Compounds Wastewater: A Review

Siti Aisyah Ishak ^{1,*}, Mohamad Fared Murshed ^{1,*}, Hazizan Md Akil ², Norli Ismail ³,
Siti Zalifah Md Rasib ² and Adel Ali Saeed Al-Gheethi ⁴

¹ School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal 14300, Seberang Perai Selatan, Pulau Pinang, Malaysia; syahisha@gmail.com

² School of Material Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal 14300, Seberang Perai Selatan, Pulau Pinang, Malaysia; hazizan@usm.my (H.M.A.); zalifahmadrasib@gmail.com (S.Z.M.R.)

³ School of Industrial Technology, Universiti Sains Malaysia, Gelugor 11800, Pulau Pinang, Malaysia; norlii@usm.my

⁴ Micro-pollutant Research Centre (MPRC), Department of Water and Environmental Engineering, Faculty of Civil & Environmental Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja 86400, Batu Pahat, Johor, Malaysia; adel@uthm.edu.my

* Correspondence: cefaredmurshed@usm.my; Tel.: +60-45996285

Received: 12 June 2020; Accepted: 11 July 2020; Published: 17 July 2020



Abstract: The utilization of various types of natural and modified polymers for removing toxicant dyes in wastewater generated by the dye industry is reviewed in this article. Dye wastewater contains large amounts of metals, surfactants, and organic matter, which have adverse effects on human health, potentially causing skin diseases and respiratory problems. The removal of dyes from wastewaters through chemical and physical processes has been addressed by many researchers. Currently, the use of natural and modified polymers for the removal of dyes from wastewater is becoming more common. Although modified polymers are preferred for the removal of dyes, due to their biodegradability and non-toxic nature, large amounts of polymers are required, resulting in higher costs. Surface-modified polymers are more effective for the removal of dyes from the wastewater. A survey of 80 recently published papers demonstrates that modified polymers have outstanding dye removal capabilities, and thus have a high applicability in industrial wastewater treatment.

Keywords: natural and modified polymer; biodegradability; toxicant dyes; industrial wastewater treatment

1. Introduction

The wastewater generated from different manufacturing processes poses serious problems for organisms and aquacultures, due to the high toxicity of these wastes, which contain different types of pollutants, such as plastic, leather, ink, fabric, palm oil, soap, pulp, and paper. These wastes are disposed of directly (with partial treatment) into the environment and natural water systems. Short-term exposure to these pollutants causes tremors and nervous system disorders, while long-term exposure causes thyroid dysfunction, weight loss, and generalized hypoxia [1]. Therefore, the treatment of the dye-containing wastewater before the final disposal is an urgent matter, not only to meet international standards, but also to protect the biodiversity in nature and to ensure the availability of pure water for future generations. The dye-containing wastewaters have been of great interest to researchers during the past several years, primarily due to the high tectorial values of the dyes, where the discharge of less than 1 ppm of a dye into the water might cause significant changes in the water's physical and chemical characteristics. The traditional treatment methods used for the treatment of wastewaters

depend mainly on chemical, physical, and biological processes (Table 1), which contribute effectively to improving the quality of the effluent parameters, such as the chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspension solids (TSS), and turbidity. Unfortunately, these methods are insufficient to remove the dyes from the wastewater. Coagulation/flocculation is a potential alternative, and a highly efficient method of removing dyes from dye-containing wastewaters.

Table 1. Advantages and disadvantages of the physical, chemical, and biological processes in dye wastewater treatment.

Process	Advantages	Disadvantages	References
Physical Process			
Ion exchange	Good surface area, effective sorbent	Not effective for all dyes, derived from petroleum-based materials, sensitive to particle charge	[2]
Adsorption	Effective for dye removal	Eco-friendly disposal of spent adsorbents, requires pretreatment, and costly maintenance	[3]
Membrane filtration	Able to remove all types of dyes	Requires proper pretreatment for SS removal, membrane fouling, expensive	[4]
Irradiation	Effective in lab settings	Requires large amounts of O ₂	[5]
Electrokinetic coagulation	Reasonable cost	High sludge problem	[6]
Chemical process			
Cucurbituril	Good sorption capacity for different types of dyes	Expensive process	[7]
Oxidation	Simple application	H ₂ O ₂ needs to be activated	[8]
Chemical coagulation-flocculation	Can remove dye molecules from dyebath effluent	High sludge production	[9]
Ozonation	Efficient for colour removal	Aldehyde by-product	[10]
Fenton's reagent	able to treat soluble and insoluble colour pigments	Results in large amounts of precipitate	[11]
Biological process			
Aerobic	Economically attractive and eco-friendly	Slow process	[12]
Anaerobic	Decolourized azo and water-soluble dyes	Produces methane and hydrogen sulphide	[13]
Decolourization by mixed cultures	Able to remove colour in 30 h	Lower efficacy, due to aerobic conditions	[14]
Decolourization by white-rot fungus	Degrades dyes using enzymes	Unpredictable enzyme production	[15]

The conventional coagulation/flocculation process, using inorganic polymers (synthetic or semi-synthetic), such as alum and ferrous sulphate (FeSO_4), could increase the environmental pollution levels by introducing non-biodegradable compounds [16]. Therefore, many researchers have shifted to using natural coagulants for wastewater treatment due to the advantages of these coagulants over chemical agents, particularly their low toxicity, low residual sludge production, and biodegradability [17]. Natural coagulants are of great interest to scientists, since they are natural, low-cost products, characterized by their environmentally friendly behaviour, and are presumed to be safe for human health [18]. However, in many of these studies, the utilization of natural coagulants was associated with the addition of natural polymers, in order to enhance the floc size by attracting smaller particles to generate much larger flocs, and, in some of the studies, natural polymers were used, without adding any coagulant, due to the high efficacies of natural polymers in the flocculation process (direct flocculation) [19,20].

The use of natural polymers (plant or animal sources) is a promising method for treating wastewater and removing dyes, due to the chemical structure and the composition of the polymers, such as the presence of many functional groups, which contribute effectively towards the removal of dyes from the wastewater. In addition, natural polymers are non-toxic, low-cost, renewable, biodegradable, and biocompatible [21]. Natural polymers are synthesized from plant products, such as starch, guar gum, gum acacia, locust bean gum, pectin, nirmali seeds (*Strychnos potatorum*), and drumstick trees (*Moringa oleifera*), as well as from non-plant sources, such as alginates, carrageenans, chitin, chitosan, bacteria, algae, and fungi [22–28]. Nonetheless, in many cases, natural polymers are not sufficient to remove the dyes from highly complex dye-containing wastewaters, containing different types of pollutants, such as heavy metals, which have a negative effect on the attraction of dyes to natural polymers. Therefore, these polymers should be subjected to a modification process, involving chemical or physical treatment, in order to increase their efficiency in removing dyes from complex wastewaters. It is vital to modify the polymers according to the target application with tailor-made specifications, designed using blending, grafting, curing or derivatization methods. The natural polymer can be chemically modified by mineral acids, bases, salts of weak acids, enzymes, acetylation, saponification, concentrated ammonium systems, and primary aliphatic amines [29]. The physical modification process includes the blending of two or more types of the polymer at an ambient temperature or elevated temperature. Polymer grafting involves the monomer being covalently bonded onto the polymeric chain, which requires a longer time compared to curing. Curing forms a coat of oligomers mixture onto the substrate using physical forces. In derivatization, the substitution of a simple molecule with a reactive group on the polymeric chain occurs to provide additional functional groups.

The current review article discusses the application of modified natural polymers in the removal of dyes from dye-containing wastewaters. The characteristics of natural polymers from plant and non-plant sources are reviewed. The feasibility of using modified natural polymers as an alternative technology for the removal of dyes from wastewater is investigated. The main aim of this article is to summarize the characteristics of dye-containing wastewaters, as well as the recent research concerning the application of modified natural polymers for the removal of dyes from different wastewaters. A comparison of several publications on the application of natural polymers has been compiled for this purpose. The authors recommend that the reported removal capacities of natural polymers be taken as a response to specific conditions, instead of maximum removal capacities.

2. Characteristics of Dyes

Over 100,000 types of commercial dye, for a total of more than 7×10^5 tons of dyestuff, are produced by the textile industries around the world annually [30]. Dyes found in the wastewater are primarily used in industrial activities, such as the textile industry and food processing. These wastes contain different types of chemicals, such as dyestuff, bleaching agents, finishing chemicals, starch, thickening agents, surface active chemicals, wetting and dispensing agents, as well as metal salts, which are used during each stage of textile production [31]. Several types of heavy metals have negative impacts on human health, as listed in Table 2 [32].

Table 2. Classes of different dyes [32].

Class	Substrates	Method of Application	Chemical Types
Acid	Nylon, wool, silk, paper, inks, and leather	Usually from neutral to acidic dyebaths	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso
Azoic components and compositions	Cotton, rayon, cellulose acetate, and polyester	Fibre impregnated with coupling component and treated with a solution of stabilized diazonium salt	Azo
Base	Paper, polyacrylonitrile, modified nylon, polyester, and inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triaryl methane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
Direct	Cotton, rayon, paper, leather, and nylon	Applied from neutral or slightly alkaline baths, containing additional electrolytes Fine aqueous dispersions often applied by using high-temperature/pressure, or lower-temperature carrier methods; dye may be padded on cloth and baked on, or thermofixed	Azo, phthalocyanine, stilbene, and oxazine
Disperse	Polyester, polyamide, acetate, acrylic, and plastics	Applied from neutral or slightly alkaline baths, containing additional electrolytes Fine aqueous dispersions often applied by using high-temperature/pressure, or lower-temperature carrier methods; dye may be padded on cloth and baked on, or thermofixed	Azo, anthraquinone, styryl, nitro, and benzodifuranone
Mordant	Wool, leather, and anodized aluminium	Applied in conjunction with Cr salts	Azo and anthraquinone
Oxidation bases	Hair, fur, and cotton aromatic	Amines and phenols oxidized on the substrate	Aniline black and indeterminate structures
Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fibre, to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone, and phthalocyanine
Sulphur	Cotton and rayon	Aromatic substrate vatted with sodium sulphide and reoxidized to insoluble sulphur-containing products on fibre Water-insoluble dyes, solubilised by reducing them with sodium hydrogen sulphite, then exhausted on fibre and reoxidized	Indeterminate structures
Vat	Cotton, rayon, and wool		Anthraquinone (including polycyclic quinones) and indigoids

Dyes are classified into anionic dyes, cationic dyes, and non-ionic dyes. Cationic dyes are a category of basic dyes, while anionic dyes are known as disperse dyes, and are comprised of acid dyes, as well as direct and reactive dyes. Cationic dyes are water-soluble, with a positive charge and high color visibility. Anionic dyes carry a negative charge and differ from cationic dyes in terms of water-solubility, structure, and ionic substituents [30]. Several different types of dye have been universally utilized in textile industries, such as azo, triphenylmethane, perylene, anthraquinone, and indigoid dyes [33]. The different types of dyes are listed in Table 3 [34]. It can be noted that many of the dyes are used in different industrial applications.

Table 3. List of heavy metal toxicities [34].

Heavy Metals	Toxicities
Arsenic (As)	Skin manifestations, visceral cancers, vascular disease
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen
Chromium (Cr)	Headache, diarrhea, nausea, vomiting, carcinogenic
Copper (Cu)	Liver damage, Wilson's disease, insomnia
Nickel (Ni)	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
Zinc (Zn)	Depression, lethargy, neurological signs, and increased thirst
Lead (Pb)	Damage to the fetal brain, kidney diseases, as well as circulatory system and nervous system diseases
Mercury (Hg)	Rheumatoid arthritis, kidney diseases, as well as circulatory system, and nervous system diseases

In addition, the dyes are subjected to chemical and physical processes during their application, which might result in the production of different, unknown secondary chemical substrates in the generated wastewater. This point is of critical concern among scientists, since new unknown chemicals are being released into the environment. Thousands of types of synthetic dyes are commercialized to obtain multicolor fabrics [32]. It is estimated that the concentration of dye effluent can be in the range of 10 to 250 mg/L [33]. However, it depends on the specific dye industry. The highest concentration of dye effluent recorded from the reactive dye industry reached 7000 mg/L [35]. Another concern associated with the traditional treatment of the dye-containing wastewater lies in the dye's unknown degradation pathway, which has resulted in the release of secondary toxic by-products into the environment and the natural wastewater, rather than being removed from the partially treated dye wastewater. The formation of chlorinated compounds and phthalic acid esters (PAEs) in the treated dye wastewater has been reported in the literature, for example, [36]. Dyes released into the environment can have acute effects on organisms, based on their level of toxicity [37]. The presence of dyed water can even be at concentrations as low as 1 mg/L [38]. This may affect the amount of light penetrating the water, reducing photosynthesis rates. Thus, it is compulsory for raw wastewater to be treated before being released into the environment. The standards and the guidelines for the disposal of textile wastewater are illustrated in Table 4. Most of the countries listed showed similar numbers for permissible pollutant concentrations to those listed by the United States Environmental Protection Agency (US EPA), with the exception of Nigeria. These pollutants were SS, Hg, As, Cu, Mn, Sn, Zn, B, Fe, Ag, Al, Se, Ba, F, formaldehyde, phenol, sulphide, oil and grease, ammoniacal nitrogen, and color. This shows that the environmental regulation in Nigeria is not strict, at least in terms of water and wastewater sustainability. Amendments to the regulations should be considered, in order to provide clean water for future generations. Jordan and Bangladesh did not list the permissible concentrations of certain pollutants, such as Cr^3 , Sn, Ag, Al, Ba, formaldehyde, and color, according to their regulations. One possible reason is that these countries follow US EPA guidelines only for several ion's discharge limits. The list shows the different concentrations of ion discharge limits except for As, Pb, Ag, Al, Se, and Ba.

Table 4. Permissible standard limits for industrial wastewater in different countries.

Parameter	Unit	Malaysia [39]	Jordan [40]	Bangladesh [41]	Nigeria [42]	Singapore [43]	US EPA [44]
Temperature	°C	40	Summer: 40, Winter: 45	Summer: 40 Winter: 45	<40	45	40
pH Value	-	5.5–9.0	6.0–9.0	6.0–9.0	6.0–9.0	6.0–9.0	6.0–8.5
BOD	mg/L	50	50	50	50	50	40
SS	mg/L	100	150	150	NL	50	TSS: 50
Hg	mg/L	0.05	0.01	0.01	NL	0.05	0.005
Cd	mg/L	0.02	0.05	0.05	<1	0.1	0.01
Cr	mg/L	0.05	0.5	0.5	<1	1	0.1
Cr ³	mg/L	0.1	NL	NL	<1	1	0.5
As	mg/L	0.1	0.2	0.2	NL	0.1	0.2
Cyanide (Cn)	mg/L	0.1	0.1	0.1	NL	0.1	0.2
Lead (Pb)	mg/L	0.5	0.1	0.1	<1	0.1	0.1
Copper (Cu)	mg/L	1.0	0.5	0.5	NL	0.1	3.0
Manganese (Mn)	mg/L	1.0	5	5	NL	5	NL
Nickel (Ni)	mg/L	1.0	1	1	<1	1	3.0
Sn	mg/L	1.0	NL	NL	NL	10	NL
Zinc (Zn)	mg/L	2.0	5	5	NL	1	2.0
Boron (B)	mg/L	4.0	2	2	NL	5	NL
Iron (Fe)	mg/L	5.0	2	2	NL	10	3.0
(xix) Silver (Ag)	mg/L	1.0	NL	NL	NL	0.1	NL
(xx) Aluminium (Al)	mg/L	15	NL	NL	NL	NL	NL
(xxi) Selenium (Se)	mg/L	0.5	0.05	0.05	NL	0.5	0.05
(xxii) Barium (Ba)	mg/L	2.0	NL	NL	NL	2	NL
(xxiii) Fluoride (F)	mg/L	5.0	7	7	NL	NL	2.0
(xxiv) Formaldehyde	mg/L	2.0	NL	NL	NL	NL	NL
(xxv) Phenol	mg/L	1.0	1	1	NL	0.2	1.0
(xxvi) Free Chloride	mg/L	2.0	600	600	600	NL	1500
(xxvii) Sulphide	mg/L	0.50	1	1	NL	0.2	2.0
(xxviii) Oil and Grease	mg/L	10	10	10	NL	10	10
(xxix) Ammoniacal Nitrogen	mg/L	20	50	50	NL	NL	50
(xxx) Colour	ADMI *	200	NL	NL	NL	7 Lovibond Units	456 nm: 7 m ⁻¹ , 525 nm: 5 m ⁻¹ , 620 nm: 3 m ⁻¹

Table 4. Cont.

Parameter		Unit	Malaysia [39]	Jordan [40]	Bangladesh [41]	Nigeria [42]	Singapore [43]	US EPA [44]
(xxxi) COD:								
(a) Pulp and paper industry								
(i)	Pulp mill	mg/L	200	200	200	150	100	250
(ii)	Paper mill (recycled)	mg/L	350	NL	NL	NL	NL	NL
(iii)	Pulp and paper mill	mg/L	250	NL	NL	NL	NL	NL
			300	NL	NL	NL	NL	NL
(b) Textile industry		mg/L	250	NL	NL	NL	NL	NL
(c) Fermentation and distillery industry		mg/L	400	NL	NL	NL	NL	NL
(d) Other industries		mg/L	200	NL	NL	NL	NL	NL

* NL: not listed.

3. Application of Polymers in Wastewater Treatment

A polymer, whether grafted as a polysaccharide base, is highly efficient at binding and linking particles to itself and vice versa during collisions, resulting in the formation of larger, more settled flocs [45]. Polymers used in flocculation and coagulation might be inorganic or organic, and might be generated from natural resources, such as tannin, pectin, sodium alginate, chitosan, cellulose, gums and mucilages, which are derived from polysaccharides and proteins [46], or synthesized, such as acrylamide based poly-(2-methacryloyloxyethyl)-trimethylammonium chloride [47–49]. However, most of the previous studies focus extensively on the utilization of natural polymers, due to their high biodegradability. Many of the natural polymers discussed in the literature have been extracted from *Moringa oleifera*, *Strychnos potatorum*, *Pseudomonas plecoglossicida*, *Spirogyra* sp., and *Aspergillus niger* [50–54]. The extraction of polymers from agro-waste, such as guar gum, pectin, tannin, and locust bean gum, is explored due to these being environmentally safe, natural compounds from renewable resources, and not producing unintended hazardous wastes [55]. The high efficiency of the natural polymers in the removal of dyes from wastewater lies in the presence of different functional groups, such as the carboxyl, hydroxyl, phosphate, amine functional groups, which can bind to the cationic charges on the dye molecules by using electrostatic force [56]. Moreover, the renewable resources are abundant, and the aspect of biodegradability attracts many researchers [57].

The studies concerning the application of natural polymers in water and wastewater treatment are listed in Table 5. Most of them were applied as adsorbents or flocculants during the coagulation and flocculation process. Natural polymers usually work best in an acidic environment. However, some studies used a pH of 8 during the adsorption, to remove the methylene blue dye with the aid of acrylic acid [58]. About 20 mg of effective material was able to remove the dye color up to 45%. The highest removal rate, at 99.2%, was accomplished at pH 2 using pectin in 34.32 mg/L of Crystal Ponceau 6R dye [59]. A natural polymer extracted from animal waste, known as chitosan, was also able to remove 99% of the Duasyn Direct dye at pH 3.4, in combination with other materials, such as polyacrylamide and bentonite, as coagulants [60]. The cellulose/polyaniline (Ce/Pn) nanocomposite removed more than 90% of Remazol Brilliant Blue R (RBBR), Reactive Orange 16 (RO), Remazol Brilliant Violet 5R (RBVR), and Reactive Black 5 (RB) from the synthetic Remazol dye effluent. In contrast, 70.23% and 80.78% of the RBBR dyestuff was removed by using a chitosan-poly (acrylic acid) conjugate in an acidic environment, at pH 4 and pH 5, respectively [61]. RBBR dyes were successfully removed (100%) by using a combination of chitosan and cross-linked chitosan.

Natural adsorbents can also minimize the reaction time. Studies of alginates showed a 50% removal of methylene blue and methyl orange, which only required 10 and 17 min to achieve, respectively [62]. Previously, researchers used an alum and *Acanthocereus tetragonus* (a cactus species) to treat synthetic water, containing 100 to 500 ppm of Congo Red and Direct Blue dye [62]. The results indicated that using *A. tetragonus* as a coagulant resulted in 90% (up to 96%) color removal, while only 80% of color was removed by the alum. In addition, two types of plant organisms, namely *Moringa oleifera* seeds and *Grewia venusta* peel, were investigated for the treatment of synthetic dyes, namely, indigo carmine (reactive dye) and methyl orange dye [63]. The *M. oleifera* seeds were more effective than the *G. venusta* peel, with 99% and 85% dye removal, respectively. Both plants also showed optimum performances in acidic environments. The *G. venusta* peel, however, required harsh acidic conditions, at pH 2, to achieve the highest removal rate. In actual textile wastewater, plant extraction was not able to decolorize the pollution when using a single coagulant. Additional assistance was required to bind the dye particles together. Inorganic iron was added to the okra mucilage at the optimum pH of 6, in order to remove 93.57% of the colorant [64]. Textile wastewater is known to be a complicated waste to process, due to the presence of both cationic and anionic charges.

Table 5. Treatment of several types of wastewater using natural polymers.

Natural Polymer	Types Of Wastewater	Treatment Process	Condition	Type Of Dye	Colour Removal	References
Pectin	Textile wastewater	Coagulation and flocculation	pH 5, 427.4 mg/l MgCl_2 and 21.9 mg/l pectin	-NA-	54.20%	[57]
	Synthetic dye	Adsorption	pectin dose 20 mg; pH 8 20 mg/l of Methylene blue	Methylene blue dye	45.00%	[58]
	Synthetic dye	Adsorption	pH 2, 247.4 mg/l dose; 34.32 mg/l dye concentration; 540-min time	Crystal Ponceau 6 R dye	99.20%	[59]
	Synthetic dye	Adsorption	no pH adjustment; 20 mg of beads was added to 50 mL of the dye solution	Methylene blue dye	1550.3 mg/g for Pectin bead and 2307.9 mg/g for pectin/cellulose microfiber bead	[60]
Chitosan	Synthetic dye	Coagulation & flocculation	pH 4.0, coagulant dose of 25 mg/l, flocculation time of 60 min and temperature of 340 K	Congo Red (CR) dye removal-	94.50%	[61]
	Synthetic dye	Adsorption	chitosan beads, 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium (pH 4.0, dose of 0.008 g, and agitation time of 20 min)	Malachite Green (MG) dye	8.07 mg g ⁻¹ and 0.24 mg g ⁻¹	[65]
	Palm oil mill effluent	Coagulation and flocculation	3 g/L alum + 0.4 g/L chitosan pH 4.51, 250-rpm rapid mixing speed for 3 min, 30-rpm slow mixing speed for 30 min, and 60 min settling time.	-	95.24%	[60]
Cellulose/Polyaniline (Ce/Pn) Nanocomposite	Synthetic dye	Adsorption process		Remazol dye effluent	95.90%, 91.90%, 92.70%, and 95.70% of RBBR, RO, RV, and RBK, respectively.	[61]
Alginate	Synthetic dyes	Activated carbon		Methylene blue and Methyl orange dyes	50.00% Methylene blue in 10 min and Methyl orange in 17 min	[62]

Table 5. Cont.

Natural Polymer	Types Of Wastewater	Treatment Process	Condition	Type Of Dye	Colour Removal	References
Acanthocercus Tetragonus (Cactus)	Synthetic dyes	Coagulation	pH 6 at dose of 5 mg/L pH 4 at dose of 6 mg/L	Congo red dye Direct blue dye	96.00% 90.00%	[62]
Moringa Oleifera Seeds (Mos)	Synthetic dyes	Adsorption	pH 5 at MOS dose of 0.5 g and 150 mg/L concentration of dye	Indigo carmine (reactive dye)	31.25 mg g ⁻¹	[63]
Grewia Venusta Peel (Gvp)	Synthetic dye	Adsorption	pH 2 at 0.5 g of GVP and 150 mg/L dye concentration	Methyl orange dye	85.00% 188.68 mg g ⁻¹	[63]
Okra Mucilage (Abelmoschus Esculentus)	Textile wastewater (during washing and finishing processes)	Coagulation and flocculation	pH 6 at 3.20-mg/L dose of Okra, and 88.0 mg/L of Fe3+	-	93.57% 5.78 mg g ⁻¹	[64]
Tannin	Synthetic dye	Coagulation and flocculation	pH 2.9 (Bentonite+ anionic flocculant) pH 2.2 (Bentonite+ anionic PAM) pH 3.4 (Bentonite+ cationic PAM) pH 2.8 (Bentonite + cationic flocculant)	Methylene blue Crystal violet Dyasyn direct dye Acid black 2	>90.00% 89.00% 99.00% 83.00%	[66]
	Manufacturing wastewater treatment	Coagulation and flocculation	-	-	99.00%	[66]
Gums C. Javahikai Seed Gum (Cj)	Synthetic dyes	Coagulation and flocculation		Direct dyes	>70.00%	[67]

Various monomers are tabulated and listed, along with some details on the dye removal rates from previous studies, in Table 6. Cationic monomers, such as poly-(2-methacryloyloxyethyl)-trimethylammonium chloride (PDMC), diallyldimethyl ammonium chloride, diethanolamine, and polyethylenimine, were very promising in thermal conditions and certain solvents. Grafting by using the opposite charges on the polymer's main backbone has a greater potential to increase the dye removal rate. A previous study showed an amphoteric grafting branch on chitosan using two monomers, known as carboxymethyl and poly-(2-methacryloyloxyethyl)-trimethylammonium chloride, for the removal of different charges of a dye molecule (cationic and anionic dyes) [68]. The existence of a quaternary ammonium group increased the cationic charges in the acidic environment, but a weak anionic character was displayed when the pH was above its isoelectric point. As the result, the bridging between these polymers and dyes became stronger. Some monomers made the polymer sensitive to pH in both acidic and basic environments. Diallyldimethyl ammonium chloride was grafted onto carboxymethyl cellulose (CMC), which was already cross-linked with mono-chloroacetic acid (MCA) and epichlorohydrin (ECH), and demonstrated a good performance in a methylene blue dye reduction, at over 98.54% removal in acidic conditions, and 83.07% removal in basic conditions, within a mere 20 min [69]. Using a PDMC monomer grafted onto carboxymethyl chitosan resulted in a 90% removal of Acid Green 25 at pH 4 and 98% of Basic Bright Yellow at pH 11. The quaternary ammonium salt was attracted to the anionic Acid Green 25 dye, producing a strong electrostatic attraction in an acidic environment, which is known as the neutralization effect. The presence of anionic charges on carboxymethyl chitosan assisted with the binding between the molecule of dye, known as Basic Bright Yellow dye, and anionic charges in the alkaline phase. A study on the alteration of bentonite with polyethylenimine to form an electrostatic charge and a hydrogen bond with the Amino Black dye, was successfully executed in an acidic environment (pH 3), at an adsorption rate of 264.5 mg/g [70]. The results showed that the mixture, containing 30% of polyethylenimine and 70% bentonite, was successfully grafted onto a molecule of (3-Glycidyloxypropyl) trimethoxysilane, with the aid of an epoxy bond, over a period of 24 h at 60 °C, in the presence of nitrogen gas.

Table 6. Examples of monomers introduced in graft copolymerization.

Monomers	Classes	Molecular Structure	Removal Percentage	References
poly(2-methacryloyloxyethyl) trimethylammonium chloride (PDMC)	Cationic		90% Acid Green 25 at pH 4	[69]
Diallyldimethyl ammonium Chloride	Cationic		98% Basic Bright Yellow at pH 11 >98.54% of methylene blue and 83.07% of anionic dye orange II pH = 4 and 11	[68]
Diethanolamine	Cationic		99.6% of Congo red, 99.8% of methyl blue, 97.5% of sunset yellow, and 81.2% of neutral red	[71]
Polyethylenimine	Cationic		Adsorption rate of 264.5 mg/g for amino black dye at pH 3	[70]
Acrylamide	Non-ionic		>99% of methylene blue at pH 10	[72]
Acrylic acid	Anionic		99.5% of Congo red and 98.7% of methylthionine chloride	[69]
Poly(glycidyl methacrylate)	Anionic		98.5% using 200 mg/L of methyl orange and methylene blue dyes	[73]
Trichloroaceticac	Anionic		Nearly 99% Rhodamine B, malachite green, and anionic dye orange were at concentration 222.6, 190.6, and 40 mg g ⁻¹ , respectively, at pH < 3	[74]

The next type of monomer, known as non-ionic monomers (such as acrylamide), have been widely grafted onto many types of polymers. One of the important steps for improving the efficiency during water treatment was to select the polymer based on the best grafting ratio. An ultrasound-assisted method was applied in order to increase the grafting efficiency since it could reduce the polymerization time. A previous study showed that sodium alginate (SAG) grafted with polyacrylamide (PAM) was able to achieve a high color removal with a grafting efficiency of 75% [72]. The highest efficiency was attained at pH 10, with a 99% adsorption of methylene blue. Recently, an in-situ ultrasonic wave-assisted polymerization was explored as a substitute for proper physical emulsion mixing. In one of the studies, the ultrasonic system was applied to anionic monomers, such as acrylic, trichloroacetic acid, and poly (glycidyl methacrylate), and showed an affinity with cationic dyes. In addition, a monomer can also help increase the pure water flux by using an acrylic monomer to reduce the graft density, which can enhance the hydrophilicity. The fabrication of polypropylene composite hollow fibre membranes with acrylic monomers demonstrated good dye retentions, with a 99.5% and 98.7% removal of Congo Red and methylthionine chloride, respectively [75]. A recent study explored the modification of a magnetic adsorbent, using poly (glycidyl methacrylate (PGMA)) microspheres, cross-linked with ethylene glycol dimethacrylate (EGDMA), in the decolorization of dyes [73]. The polymerization techniques were modified, to some extent. A modified multi-step swelling polymerization method was employed with iminodiacetic acid (IDA) used to produce carboxyl groups, and the magnetic traits were successfully embedded inside the microsphere's pore using in-situ chemical co-precipitation. The coating microspheres were then exposed to ultraviolet (UV) radiation. The results indicated a good adsorption rate, and the decolorization rate reached 98.5%. The decolorization efficiency was more than 80%, despite the adsorption–desorption cycle being run ten times. Other monomers, such as trichloroacetic acid, remove 99% of cationic dyes, such as malachite green and rhodamine B [74]. High adsorption capacities were recorded for rhodamine B, at 222.6 mg/g, and 190.6 mg/g for malachite green. A low adsorption rate was detected for anionic orange dye, at 40 mg/g, due to a smaller number of cationic charges on the adsorbent.

Current research focuses on the extraction of microbial polymers, since it is easy to carry out, and cost effective for industries. In order to obtain highly effective polymers for use in the removal of dyes, researchers have focused on the polymers generated from indigenous microbes, such as *Pseudomonas pseudoalcaligenes*, *Pseudomonas plecoglossicida*, and *Staphylococcus aureus*, in fawn dyes, medibblue, whale dyes, and mixed dyes [76], because these dyes have a high resistance to decolorization. This is possibly due to the acidic nature of these dyes, which makes it difficult for them to be absorbed by microbial polymers [77]. The indigenous microbes might have adopted and developed a resistance mechanism in order to survive in these dyes, therefore, these organisms exhibit a high dye removal efficiency. In a recent study, one bacteria species (*Brevibacillus laterosporus*) and one yeast species (*Galactomyces geotrichum*) were immobilized in a stainless-steel sponge and in polyurethane foam. The microbial consortia successfully decolorized 50 mg/L of Remazol Red dye in the stainless-steel sponge and in the polyurethane foam in 11 h and 15 h, respectively [78]. Immobilization by using calcium alginate and polyvinyl alcohol produced more consistent results but required more time to complete the decolorization process at 20 h in the stainless-steel sponge and 24 h in the polyurethane foam. In another study, nine different bacterial strains from textile wastewater and sludge were isolated, which resulted in one *Planococcus* sp. with decolorization abilities being found in textile wastewater [79]. The *Planococcus* sp. decolorization ability was increased to 78% by combining it with a 55% peptone and a 60% dextrose solution (in a nitrogen and a carbon source, respectively).

4. Graft Polymer (Coagulant/Flocculant)

New developments in the polymer research have drawn attention towards graft polymers, also known as grafted copolymers. The advantages of graft polymers include their non-toxicity, high biodegradability in nature, and low cost (Figure 1). Moreover, their high molecular weights,

as well as the existence of new branching on the molecular chains, makes them more suitable for removing dyes from wastewater. Natural graft polymers are defined as additional polymers inserted into the backbone of a natural polymer, in order to alter the molecular chain. The alteration extends the natural polymer's length, thus improving the adsorption of molecules with opposite charges in the solution [80]. Moreover, the existing branches of natural polymers have been modified in many studies, by inserting an acetyl group into the chitosan, resulting in more functional groups being added to the polymeric chain, thus improving the absorbance capacity of the polymers for azo dyes from wastewater [81]. The formation of the carboxylic group on the chitosan's polymeric chain was able to remove cationic and anionic dyes, which in this case involved the synthetic methylene blue and methyl orange dyes. As reported by the previous study, the grafted surface of graphene oxide showed a good potential for dyes due to the presence of carboxylic and hydroxyl groups that produce a colloidal dispersion in the aqueous medium due to its hydrophilic nature [82]. To conclude, the existence of the carboxylic group was indeed helpful in removing the dye particles.

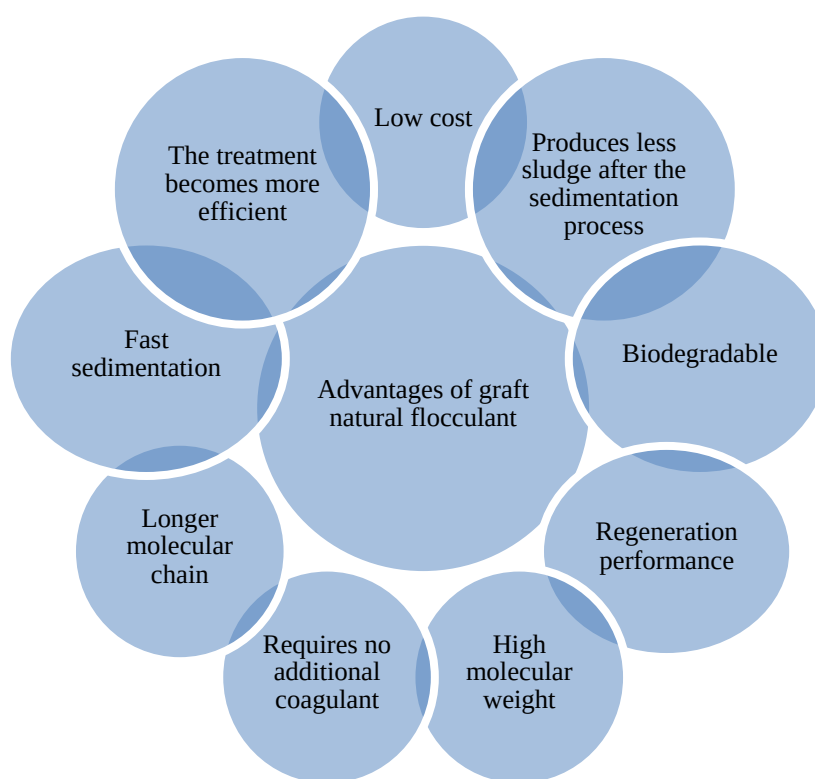


Figure 1. Benefits of grafting a natural polymer.

In order to better understand graft polymers, further studies on their mechanisms are required. The two mechanisms involved in graft polymers are charged neutralization and bridge aggregation. Several insoluble complexes form at higher speeds during rapid mixing, indicating that neutralization has occurred. Subsequently, bridging occurred, resulting in the aggregation of the insoluble complexes and contributing to the formation of larger flocs, due to the increase in the molecular weight [83]. The links in the large flocs settled down rapidly, followed by those in the smaller flocs. A study showed that the bridging effect was more beneficial to the flocculation of grafted natural polymers than for linear polymers [84]. Figure 2 demonstrates the differences in natural polymer branching before and after modification [83]. Different particles are adsorbed onto the grafted natural polymer's chain to form bridges, which link to the opposite charges and occupy freer binding sites. Natural graft polymers carry more binding sites as the length of the modified natural polymer is longer than the original length [85].

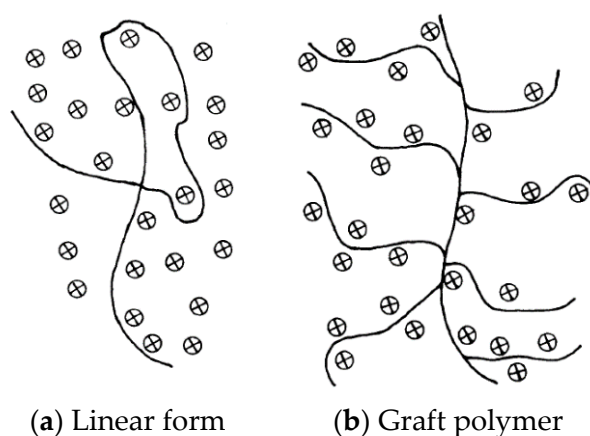


Figure 2. (a) Linear polymer represents the coil form bound to the oppositely charged particles, while (b) is the graft polymer presenting the comb form, able to bind to a large number of oppositely charged particles in the solution [83].

4.1. Factors Affecting the Efficiency of Polymer Coagulants

4.1.1. Type of Coagulant

The current trends in wastewater coagulation research focus mainly on the utilization of biodegradable polymers, such as chitosan, *Moringa oleifera*, nirmali seeds, and cactuses [86]. Natural polymers are used as coagulants because they are derived from renewable resources, biodegradable, cheap, non-toxic, and able to minimize the sludge production at the end of the treatment, as well as prevent the health risks associated with the utilization of alum, such as Alzheimer's disease [87]. Nonetheless, the study authors stated that synthetic organic polymers, such as diallyldimethyl ammonium chloride, as well as copolymers of quaternized dimethylaminoethyl acrylate or methacrylate, exhibited a better performance in the coagulation processes, due to charge densities and molecular masses [88]. The advantages of the synthetic organic polymers include the slow degradation activity, compared to that of the natural polymers with a longer life span, as well as the high charge density and molecular mass, which make them effective coagulants [89]. The disadvantages of synthetic polymers were not only their hydrophilic nature, but also their high cost [90]. This resulted in extra care being required during storage and transportation. Other drawbacks included limited molecular weight and dosage scale, which narrowed down the application range, and the presence of poisonous monomers, which are non-biodegradable and can be hazardous to the environment [91]. Although the wastewater treatment becomes more effective with an increase in dosage, problems arise when synthetic polymers are used due to unreacted chemicals making up the monomer unit (e.g., formaldehyde), as well as unreacted monomers (e.g., diallyldimethylammonium chloride and acrylamide) and reaction by-products.

4.1.2. Coagulant Concentrations and Mixing Conditions

A sufficient amount of coagulant should be dispersed completely in the wastewater, with the optimum mixing speed and time, in order to get the maximum contact between the coagulant and the suspended particles. One of the main factors affecting a coagulant's efficiency is its concentration. It has been demonstrated that coagulants with a cationic charge neutralize the suspensions and destabilize the colloids. Increasing a polymer's concentration improves its performance, however, a high dosage has a negative effect on the coagulation processes and restabilizes the colloids, reversing the charge and reducing the removal rate [92]. A previously published study proved that increasing the organic coagulant concentration increased the COD removal rate, which, in this case, involved a combination of *Moringa oleifera* and potassium chloride. Using aluminium sulphate had the opposite effect [93]. The removal of organic matter declined as the concentration of hydrolysed metal salt increased.

The hydrolysed metal salt can contribute to coagulation by adsorption [94]. However, the reversal of charge on the colloidal particle is the reason why the removal rate decreased. The aim of adding the salt to the natural polymer was to aggregate the particles, by means of a double layer compression [10]. The excessive addition of salt may also reduce the removal rate, due to the reduction in protein solubility (the salting-out effect) and the effect of hydration [95].

On the other hand, the mixing processes can also increase the removal rate efficiencies. The two phases that involve the mixing parameters in the coagulation are rapid mixing and slow mixing. The speed limit and the duration of time also play a role. The purpose of the rapid mix phase is to disperse the coagulant well, in order to stimulate particle collisions by using a power paddle. Rapid mixing was applied in a study, at speeds ranging from 80 rpm to 400 rpm and for time periods ranging from 0.1 min to 8 min. By varying rapid mixing, the formation, the breakage, and the regeneration of floc can be determined. A study showed that each coagulant has its own rapid mix condition [96]. An aluminium-based coagulant, for example, required the minimum time period to form a larger floc during the rapid mix phase, but the maximum time was needed when using a cationic polyelectrolyte [97]. Somehow, the regrowth of flocs after longer time periods was possible when using the cationic polyelectrolyte. The alum-based coagulant, on the other hand, had an irreversible effect on the floc recovery after the breakage. In agreement with other studies, mixing at 120 rpm for half a minute is required, in order to form larger flocs of highly turbid water [98]. The study also found that rapid mixing was connected to slow mixing, due to the flocs' resistance throughout the slow mixing phase. The time requirement during mixing did not appear to be the primary factor in removal effectiveness. The study found that the efficiency of coagulation, in terms of color and turbidity, had an indirect effect on the time [99]. However, the application of these factors during the process can provide some additional data. The following phase of slow mixing can take place at speeds ranging from 10 rpm to 60 rpm, for time periods ranging from approximately 5 min to 30 min. The investigation indicated that a slow mixing intensity had a beneficial effect on the charge neutralization coagulation when compared to sweep flocculation. Based on the optimum conditions, longer time periods are required during slow mixing, in order to produce larger flocs. During charge neutralization, an extended slow mixing phase can help to boost the coagulation performance, in case of inadequate rapid mixing [100]. This is in contrast with the sweep flocculation mechanism, where a shorter period of time is required for the slow mixing phase if the rapid mixing is excessively long. The mixing process should be followed by a sufficiently long settlement process [101]. Having larger flocs can shorten the time required for the settlement. Thus, the formation of larger flocs is important in the coagulation process.

4.1.3. Functional Groups

Polymeric coagulants contain several types of functional groups with negative charges, such as hydroxyl (OH^-), amine (NH_3^-), phosphate (PO_4^-), and carboxyl (COO^-). These groups have bridging effects on the particles with opposite charges in the water and the wastewater [102]. In nirmali seeds, the presence of OH^- groups along the galactomannan and the galactan molecular chains provide abundant attachment sites for interparticle bridging. The presence of the hydroxyl group, indicated by a broad wave between 3100 and 3500 cm^{-1} , can be observed for natural polymers. Previous studies on different polymer analyses of functional groups are summarized in Table 7.

Table 7. Summary of the functional groups on selected polymers.

Polymers	Functional Groups
Chitosan	Chitosan was identified by the presence of OH groups, with NH band overlapping around 3300 cm^{-1} ; with additional NH stretching vibrations at 1649 cm^{-1} and 1578 cm^{-1} , and C-O bonds appearing at 1419 cm^{-1} and 1378 cm^{-1} , due to the presence of remaining acetylated moieties of chitin [103].
Tannin	Tannin can be recognized by the vibration of phenolic hydroxyl group, identified by peaks at $3200\text{--}3700$ and 1325 cm^{-1} . The C-O aromatic ring and the C-C stretching vibration were observed at 1204 and 1536 cm^{-1} , respectively. The absorption peak between 1000 and 1150 cm^{-1} was associated with ethers (C-O-C) [103].
Moringa oleifera	Moringa oleifera spectrum showed the absorption of OH stretching at 3400 cm^{-1} ; symmetric stretching of C-H at 2925 cm^{-1} ; carboxylic group (COO^-) stretching bands at 1610 cm^{-1} and 1451 cm^{-1} , and carbonyl group (C=O) stretching at 1070 cm^{-1} [104].
Zinc oxide nanoparticles	The absorption of a large number of hydroxyl groups is indicated by the broad peak between 3500 and 3100 cm^{-1} ; and Zn-O bond stretching is indicated by the lower absorption peak $< 600\text{ cm}^{-1}$ [105].
Polyacrylamide	Polyacrylamide spectrum demonstrates broad absorption bands at 3421 and 3192 cm^{-1} , indicating N-H stretching vibrations. The absorbance peaks at 1655 cm^{-1} correspond to the asymmetric C=O stretching vibrations [106].
Graphene oxide	Common absorption bands, observed at 3387 cm^{-1} , are ascribed to -OH stretching vibrations. The C=O groups ($-\text{COOH}$), the C=C stretching, the C-O-C stretching, and the C-O (C-OH) stretching peak can be seen at 1730 , 1621 , 1224 , and 1049 cm^{-1} , respectively [106].
Sodium alginate	Hydroxyl absorption peak was recorded at 3421 cm^{-1} ; asymmetric and symmetric stretching vibrations of carboxylic groups were observed at the peaks near 1621 cm^{-1} and 1395 cm^{-1} [106].
Carboxymethyl cellulose	Carboxymethyl cellulose (CMC) can be identified by the wide spectra associated with ether bonds at absorption peaks between 1000 and 1100 cm^{-1} . The absorption band at 1588 cm^{-1} was attributed to the scissoring mode of the carboxylic groups (COO^-) [73].
Pectin	Pectin absorption band were indicated by five bands at 1019 , 1052 , 1076 , 1104 , and 1149 cm^{-1} . Meanwhile, other bands at $1350\text{--}1750$ were associated with carboxylic groups and C=O stretching in the protonated carboxyl group. In addition, two bands, representing symmetric and asymmetric stretching modes in carboxylic group at $1600\text{--}1650\text{ cm}^{-1}$ and $1400\text{--}1450\text{ cm}^{-1}$, respectively. In addition, the ether and the C-C bond included in the molecule of pectin were indicated by the absorption bands between 1100 and 1200 cm^{-1} [107].
Locust bean gum	The previous spectrum showed a broad peak at 3311 cm^{-1} , which is assigned to the O-H group. The presence of sharp peaks at 1004 cm^{-1} was attributed to C-O-H vibrations [108].

Biopolymeric flocculants, such as pectin, have similarly negative charged particles (OH and COO) [109] with longer chains, resulting in electrostatic repulsion, due to the chains stretching out [110,111]. Studies on Polydiallyldimethylammonium chloride (PDADMAC) grafted onto a locust bean gum showed the adsorption of amino groups reacting with anionic dye particles, indicated at 1474 and 3022 cm^{-1} on the spectrum, increased with time, until the adsorption equilibrium was reached at approximately 600 min [112]. Other studies on the existence of phenolic groups in tannin structures showed these groups undergoing deprotonation to produce phenoxide effortlessly, thus expanding the oxygen atom's electron density [103]. The efficiency of the coagulation process is enhanced by the presence of additional phenolic compounds in the polymer structure [81]. The studies have shown that phenolic and amine groups are accessible in commercial tannin, which is a cationic polymer, with single tertiary amine groups present in each monomer [113]. Natural polymers can be grafted onto the surface of graphene oxide (GO) for the removal of dyes as GO has show a good potential for the removal

of dye from aqueous solutions, as investigated by experimental and computational methods [82]. The computational evidence was illustrated using visual molecular dynamic programmes as can be seen in Figure 3. The surface area of graphene oxide posed a more negative charge in low pH with the absence of salt, which resulted in a protonated carboxylic group since no sodium ion (Na^+) can attach to the surface. Otherwise, an anionic group (CH_3COO^- , SCN^- , SO_4^{2-} , NO_3^-) was able to attach to the hydrophobic graphene oxide. A previous study claimed that the higher surface area assisted the graphene oxide's ability to interact with direct blue Indosol dyes (a subcategory of anionic dyes) at $\text{pH} < 4$, due to several factors, such as the presence of hydroxyl, carboxylic, and oxygen groups, as well as the active sites on the dye particles, which may have resulted in stronger chemical bonds between the graphene oxide and the dyes [114]. Instead, Direct Red 81 was added to solutions with higher pH values (>7.5), resulting in nearly 100% removal. The new hydroxyl group will interact with amine groups from dye particles in basic conditions, increasing the adsorption observed in studies. In addition, multiple layers of neutralized sulphonate groups in the dye are formed, due to the electrostatic interaction between the oxygen-containing functional groups on the graphene oxide. In addition, the pi interaction and the bonding with the hydrogen molecules also help to increase the adsorption rate.

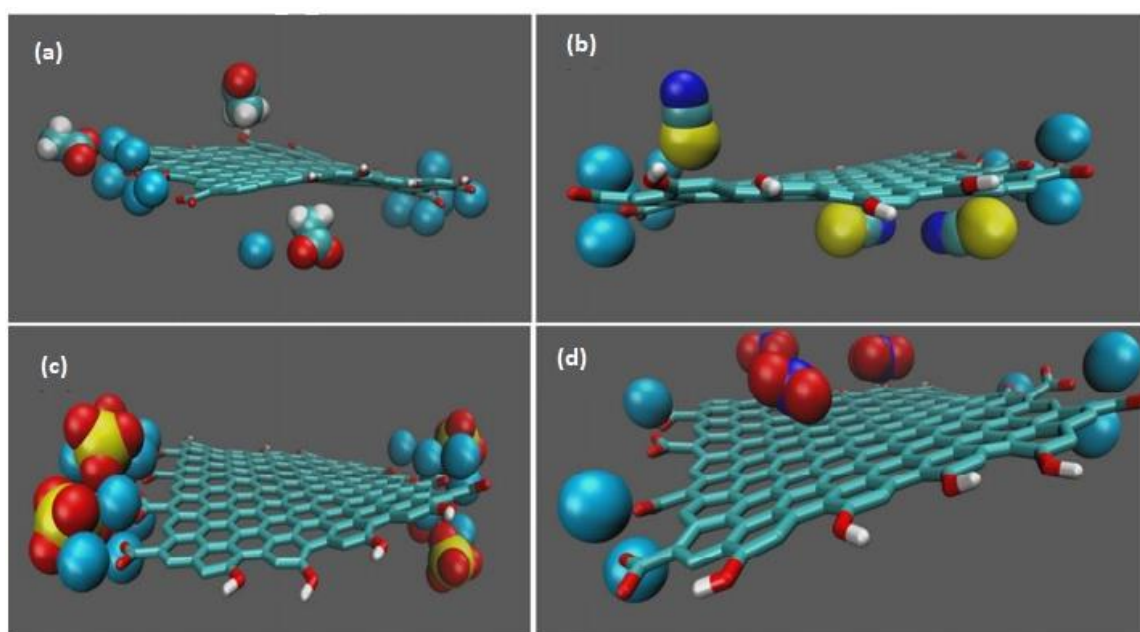


Figure 3. Visual molecular dynamics simulation of the attachment between graphene oxide (GO): (a) CH_3COO^- ; (b) SCN^- ; (c) SO_4^{2-} and (d) NO_3^- . Color coding: C-cyan, O-red, N-dark blue, H-white, S-yellow, Na-light blue [82].

4.1.4. Molecular Weight (MW) of the Flocculant/Coagulant Aid

Different polymers have different molecular weights, based on their molecular structures. The molecular weight of the flocculant added after the coagulant has a significant impact on the process. Polymers with higher molecular weights contribute to efficient toxin removal, due to the mechanisms involved, such as charge neutralization, bridging, and electrostatic patch. Negatively charged particles are destabilized by the Van der Waals forces, due to the presence of elements with high molecular weights and numerous positive charges [110]. As soon as the Van der Waals forces are balanced out by repulsive electrostatic forces, flocs begin to develop. In addition, larger loops and ends form as the molecular weight increases; consequently, more sites are available to attract suspended particles [115]. Polymers with a minimum molecular weight of 800,000 daltons are more suitable for bridging [116]. A study of anionic polyacrylamides with different molecular weights indicates that a larger equivalent

size (resulting from a higher molecular weight being added at an extremely rapid mixing rate), results in a faster settling time [117]. However, a higher dosage is required to increase the density and to shorten the settling time, by using a lower molecular weight. Polymers with higher molecular weights and more branched chains demonstrate a better color removal performance and faster settling rates than linear chains with small numbers of active sites for the pollutant to bind [118]. A high resistance and large flocs simulated the separation of the pollutant particles out of the solution and their subsequent sinking to the bottom. The adsorption of the target pollutant requires a strong adhesion between solid–liquid interfaces, which is influenced by the polymer’s molecular weight [119]. In another study, lignin- [2-(methacryloyloxy) ethyl] trimethyl ammonium chloride (METAC), with a high molecular weight, was more successful at removing Reactive Orange 16 than Reactive Black 5, though both dyes are anionic azo dyes [120]. The polymerization of polyacrylamides, with gelatine used as a tested stabilizer, shows a lower dye removal potential when using a low molecular weight grafted polymer [121]. The Congo Red dye removal was compared when using a copolymer (PAB) before and after grafting with dextran (DAB), and the experiment showed a 68.1% removal rate when using DAB, compared to 40.9% without the DAB, due to the higher molecular weight of the DAB grafted polymer [122]. Using a commercial polymer, such as polyaluminium chloride (PAC), achieves a 48% removal rate. This indicates that the molecular weight does influence the effectiveness of the coagulation, as well as the flocculation performance.

4.1.5. Type of Charge Density

A polymer’s charge density is categorized into low, medium, and high, based on the percentage mole of the ionic group (10%, 25%, and 50–100%, respectively) [123]. A low charge density enhances the polymer’s bridging effect. The effectiveness of the charge density ranges from 5% to 15% and can improve shear resistance with higher molecular weights. Introducing graft copolymers results in an improved stability and extends the biodegradability, to some extent [124]. In addition, re-flocculation is incomplete when the charge density is below 12. The optimum flocculant concentration has been found to be dependent on the ionic strength [125]. Adding cationic charge polymers significantly enhances the coagulating capabilities. This effect increases in the order of monovalent < bivalent < trivalent. For example, adding the trivalent ion results in a stronger floc structure, and increases the floc size, the density and the shear resistance to a greater extent compared to monovalent ions [126]. One study, comparing four different lignin-based polymers extracted from pulping sludges, showed an excellent removal rate of disperse dye wastewater when higher-charge-density polymers were used. Particles form larger agglomerates when high-charge-density polymers are utilized, while looser molecules, despite the abundance of active sites for the dye molecule to attach, undergo slower reactions, as a consequence of the steric bulk [118].

5. Removal of Dyes by Using Modified Natural Polymers

Modified natural polymers have gained more attention in the recent years. Different types of compounds have been used to modify natural polymers for the purpose of removing dyes from wastewaters—for example, ammonia, formaldehyde, zinc oxide nanoparticles, lignosulfonate, carboxymethylstarch, polyacrylamide and various monomers [127]. The studies concerning modified natural polymers are presented in Table 8.

Table 8. Compilation of toxicant removal from several types of wastewater using modified polymers.

Graft Polymer (Modified)	Additional Compound	Types of Wastewater	Treatment Process	Response	Percentage Removal (%)	References
Amine Modified Tannin Gel Mw: Na	Aqueous ammonia	Synthetic wastewater, using Brilliant green dye	Adsorption	Colour removal	94.05	[47]
Tannin Extracts (<i>Acacia Mearnsii</i> De Wild And <i>Schinopsis Balansae</i>) Mw: Na	Clarotan with diethanolamine and formaldehyde	Guadiana River, in Badajoz (south-western Spain)	Coagulation and flocculation	Turbidity removal	>90.00	[128]
Chitosan—TiO ₂ Nanoparticles	Titanium dioxide nano particles	Simulated textile wastewater	Coagulation and flocculation	Removal of Cd, Cu, and Pb	<97.00	[129]
Chitosan Modified With CHPATC	Cationic moiety N-3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) in presence of sodium hydroxide	Simulated laundry wastewater	Coagulation and flocculation	Colour Turbidity	76.20 90.94	[130]
Cationic Amylopectin Mw: 6.89 × 10 ⁴ g/Mol					78.00	
Cationic Amylose Mw: 2.64 × 10 ⁶ g/Mol					50.00	
Cationic Chitosan Mw: 1.2 × 10 ⁵ g/Mol					>80.00	
Cationic Glycogen 6.81 × 10 ⁶ g/Mol	-	Synthetic reactive black dye	Adsorption	Colour removal	96.20	[67]
Cationic Guar Gum Mw: 6.6 × 10 ⁵ g/Mol					70.00	
Cationic Starch Mw: 4.32 × 10 ⁵ g/Mol					65.00	
Cationic Tamarind Kernel Polysaccharide Mw: 6.12 × 10 ⁶ g/Mol					82.00	

Table 8. Cont.

Graft Polymer (Modified)	Additional Compound	Types of Wastewater	Treatment Process	Response	Percentage Removal (%)	References
Cassia Javahikai Seed Gum-Grafted Polyacrylamide (Cjg), Mw: Na	Polyacrylamide PAM	Textile wastewater effluent	Coagulation and flocculation	Colour removal Total suspended solid	35.00 80.00	[67]
Tannin-Based Hydrogel Mw: Na	Grafted Copolymer of Allyl Glycidyl Ether with Acrylamide	Synthetic heavy metal	Adsorption	Lead (Pb) removal	99.00 at (0.5 mmol/L)	[131]
Carboxymethyl Chitosan Grafted Polyacrylamide (Cmc-G-Pam) Mw: Na	Grafted polyacrylamide	Synthetic dye Methyl orange (anionic dye) Basic right yellow (cationic dye)	Coagulation and flocculation	Colour removal	93.00	[132]
Lignosulfonate–Acrylamide–Chitosan	Grafted with lignosulfonate and acrylamide	Acid blue 115 Reactive black 5 Methyl orange	Flocculation	Colour removal	>95.0 >95.0 >50.0	[133]
Hydroxypropyl Methyl Cellulose, Grafted With Polyacrylamide (Hpmc-G-Pam) Mw: Na	Grafted polyacrylamide	Raw mine wastewater	Coagulation and flocculation	Turbidity	95.00	[83]
Hydrolysed Polyacrylamide-Grafted Carboxymethyl starch (Hyd. Cms-G-Pam) Mw: Na	Grafted Carboxymethyl starch	Textile wastewater	Coagulation and flocculation	Colour removal	88.18	[28]
Polyacrylamide-Grafted Sodium Alginate Mw:Na	Grafted sodium alginate	Synthetic dye	Adsorption	Colour removal	99.00	[134]
Chitosan-Acrylamide-Fulvic Acid (Camfa)	Grafted with acrylamide and fulvic acid	Methylene Blue Acid blue 113, reactive black 5 and methyl orange	Adsorption	Colour removal	99.00 97.00 91.60	[135]

Table 8. Cont.

Graft Polymer (Modified)	Additional Compound	Types of Wastewater	Treatment Process	Response	Percentage Removal (%)	References
Polyethylenimine-Grafted Cellulose Mw: Na	Grafted with Cellulose	Silk printing and dyeing wastewater	Flocculation	Total suspended solid	38.20	[136]
				(TSS)	73.40	
				COD	95.70	
				reductionTurbidity		
				Total suspended solid	87.40	
				(TSS)	96.20	
Bamboo Pulp Cellulose Grafting Polyacrylamide (Bpc-G-Pam)	Grafted with polyacrylamide	Cationic and disperse dye	Flocculation	Colour removal	79.90	[137]
					97.00	
Carboxymethylcellulose-G-Poly[(2-Methacryloyloxyethyl) Trimethyl Ammonium Chloride] (Cmc-G-Pdmc)	graft poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride]	Machining wastewater Acid green 25	Coagulation and flocculation	Colour removal	93.50	[69]
Pafc-Starch-G-P(Am-Dmdaac)	graft copolymer with acrylamide and dimethyl diallyl ammonium chloride	Brilliant blue KN-R Yellow M-3RE Dark blue M-2GE Green KE-4B	Coagulation and flocculation	Colour removal	97.30	[138]
					89.70	
					83.00	
					85.00	

Previously, researchers would come up with effective grafting procedures involving natural polymers. For example, an amine-modified tannin gel effectively removed brilliant green (at 94.05%) in neutral pH conditions, using the external surface adsorption mechanism [47]. In another study, a tannin-based polymer was grafted onto tannin extracted from *Schinopsis balansae* and *Acacia mearnsii* de Wild, by running a Mannich base reaction [139]. A tannin extract, modified with Clarotan and diethanolamine, was first acknowledged for its potential use as a dye or a surfactant in wastewater and river water [71]. Based on the wastewater simulation test, about 92% of the dye could be removed from a 100 mg/L stock solution, and the surfactant concentration could be reduced from 50 to 7.5 mg/L using a 150 mg/L stock solution. Modified tannin can perform well in water and wastewater treatment processes, as shown by previous studies [140,141]. Another study, focusing on lead adsorption, showed the ability of tannin-based hydrogels to absorb metal elements on their surfaces well [131]. When grafted onto a well-known chitosan, (3-chloro 2-hydroxypropyl) trimethylammonium chloride was used to reduce 1000 mg/L of the melanoidin dye at pH 3 using a 3 g/L dose chitosan-g-CHPTAC, which was able to remove up to 76.2% of the color and 90.14% of the turbidity [130]. A study by Sanghi et al. [67] focuses on grafting polyacrylamides onto different types of polysaccharides, such as amylose, amylopectin, starch, tamarind kernel, guar gum, glycogen, and chitosan. Grafted glycogen, having the highest molecular weight (6.81×10^6 g/mol) and radius of gyration, was the most effective, adsorbing 96.2% of the dyes, due to more branching taking place on the glycogen's backbone. This showed that the molecular weight is related to the effectiveness of the treatment. In a previous study, carboxyl methyl chitosan-graft-polyacrylamide (CMC-g-PAM) exhibited a high efficiency (above 90%) in removing anionic and cationic dyes. An investigation of ternary graft polymers revealed a high decolorization performance when using grafted chitosan for removing anionic and neutral dyes but demonstrated a low efficiency for the removal of cationic dyes [132].

Recent studies have demonstrated that acrylamide grafted onto sodium alginate successfully removes the methylene blue dye, with a removal rate of 99%. The sodium alginate alone did not remove any of the dye at all. However, there are some limitations of using modified natural polymers to treat real textile wastewater, due to the presence of different organic and inorganic complex chemicals. For example, grafted carboxymethyl starch was only able to remove 88.18% of the detected color at 520 nm [28]. The percentage removal of a synthetic dye can reach nearly 100%, but not in real textile wastewater. Grafted cellulose was used for the treatment of silk printing and dyeing wastewater, achieving a 95.7% removal of the COD [136]. The attachment of cellulose onto hyperbranched polyethylenimine resulted in a highly effective removal of ammonia nitrogen, total iron, and total phosphorus, at the original pH. The effluent pH did not require any adjustment, being approximately neutral. This characteristic is an additional benefit of polymer grafting, as the pH values during coagulation and flocculation treatments are independent of one another. Another study reported a wide pH range (from pH 5 to pH 9) available for the treatment of Acid Blue 113 and Reactive Black 5, which happened to remove more than 90% of the dye colors [135]. In addition, increasing the grafting ratio also increases the floc size and compactness, resulting in a lower dosage being required, in order to achieve a higher color removal efficiency. A cellulose-based flocculant, combined with poly-(2-methacryloyloxyethyl)-trimethylammonium chloride, showed the best removal rate for an anionic dye (97.3%). Increasing the grafting ratio also improved the color removal rate. Moreover, other advantages of grafted polymers depend on the dosage applied during the process, which can be reduced up to 50% in synthetic wastewater using PAFC-Starch-g-p (AM-DMDAAC) [138]. With increasing environmental awareness, a recent study demonstrated the outstanding biodegradability of cellulose, extracted from bamboo pulp, grafted with polyacrylamide, at 66.5% and 67.6% after 45 d and 90 d, respectively, in a soil-extracting solution [137]. It was also successful at removing organic dyes, such as cationic and disperse dye solutions, with an average removal rate of 97%. Overall, grafted natural polymers showed a superior dye removal performance, compared to natural polymers on their own.

6. Conclusions

Over the past several decades, high levels of toxicants have been produced as the result of dye wastewater treatment involving harmful chemicals. Even though factors like turbidity, color, COD, BOD, and the levels of heavy metals have been reduced to meet the permissible standards, the sludge produced as the result of the treatment still comes into contact with toxic materials. Thus, an effective solution is required in order to improve water quality. Grafted natural polymers could replace commercial polymers, with an additional incentive of reduced costs. The characteristics of effective coagulants can be enhanced by using specific types of polymers, the concentration and mixing conditions, functional groups, higher molecular weight, and charge density according to the target dyes pollutant. The chemical modification of polymers provided the opportunity to explore beyond conventional applications. A thorough understanding of the polymer and its chemical modification has a vast potential to be the future trend for the use of cosmetics, pharmaceutical, food, leather, paper, and textile industries.

Author Contributions: Conceptualization, S.A.I., H.M.A. and A.A.S.A.-G.; methodology, S.A.I. and S.Z.M.R.; resources, S.A.I.; writing—original draft preparation, S.A.I.; writing—review and editing, S.A.I.; supervision, M.F.M., A.A.S.A.-G., and N.I.; funding acquisition, M.F.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by RUI grant no. 1001/PAWAM/814259.

Acknowledgments: The authors would like to thank the Malaysian government for providing Mybrain15 scholarship and thankful for the kind support of staff of the Universiti Sains Malaysia.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Uppal, H.; Tripathy, S.S.; Chawla, S.; Sharma, B.; Dalai, M.K.; Singh, S.P.; Singh, S.; Singh, N. Study of cyanide removal from contaminated water using zinc peroxide nanomaterial. *J. Environ. Sci.* **2017**, *55*, 76–85. [[CrossRef](#)] [[PubMed](#)]
2. Crini, G.; Lichtfouse, E.; Wilson, L.D.; Morin-Crini, N. Adsorption-Oriented Processes Using Conventional and Non-Conventional Adsorbents for Wastewater Treatment. In *Green Adsorbents for Pollutant Removal*; Springer: Cham, Switzerland, 2018; pp. 23–71.
3. Othmani, A.; Kesraoui, A.; Boada, R.; Seffen, M.; Valiente, M. Textile Wastewater Purification Using an Elaborated Biosorbent Hybrid Material (Luffa-Cylindrica-Zinc Oxide) Assisted by Alternating Current. *Water* **2019**, *11*, 1326. [[CrossRef](#)]
4. Zhan, Y.; Wan, X.; He, S.; Yang, Q.; He, Y. Design of durable and efficient poly (arylene ether nitrile)/bioinspired polydopamine coated graphene oxide nanofibrous composite membrane for anionic dyes separation. *Chem. Eng. J.* **2018**, *333*, 132–145. [[CrossRef](#)]
5. Arcanjo, G.S.; Mounteer, A.H.; Bellato, C.R.; da Silva, L.M.N.; Dias, S.H.B.; da Silva, P.R. Heterogeneous photocatalysis using TiO₂ modified with hydrotalcite and iron oxide under UV-visible irradiation for color and toxicity reduction in secondary textile mill effluent. *J. Environ. Manag.* **2018**, *211*, 154–163. [[CrossRef](#)]
6. Xu, Y.; Li, Z.; Su, K.; Fan, T.; Cao, L. Mussel-inspired modification of PPS membrane to separate and remove the dyes from the wastewater. *Chem. Eng. J.* **2018**, *341*, 371–382. [[CrossRef](#)]
7. Rai, A.; Chauhan, P.S.; Bhattacharya, S. Remediation of Industrial Effluents. In *Water Remediation*; Springer: Singapore, 2018; pp. 171–187.
8. Maria, G.; Yolanda, M.D.; Roberto, T.P.; Manuel, L.J.; Gumersindo, F.; Teresa, M.M. Textile Wastewater Treatment by Advanced Oxidation Processes: A Comparative Study. In *Life Cycle Assessment of Wastewater Treatment*; CRC Press: Boca Raton, FL, USA, 2018.
9. Saritha, V.; Srinivas, N.; Vuppala, N.S. Analysis and optimization of coagulation and flocculation process. *Appl. Water Sci.* **2018**, *7*, 451–460. [[CrossRef](#)]
10. Ghuge, S.P.; Saroha, A.K. Catalytic ozonation of dye industry effluent using mesoporous bimetallic Ru-Cu/SBA-15 catalyst. *Process Saf. Environ.* **2018**, *118*, 125–132. [[CrossRef](#)]

11. Nasuha, N.; Ismail, S.; Hameed, B.H. Activated electric arc furnace slag as an effective and reusable Fenton-like catalyst for the photodegradation of methylene blue and acid blue 29. *J. Environ. Manag.* **2017**, *196*, 323–329. [\[CrossRef\]](#)
12. Manavi, N.; Kazemi, A.S.; Bonakdarpour, B. The development of aerobic granules from conventional activated sludge under anaerobic-aerobic cycles and their adaptation for treatment of dyeing wastewater. *Chem. Eng. J.* **2017**, *312*, 375–384. [\[CrossRef\]](#)
13. Rodríguez, R.; Espada, J.J.; Molina, R.; Puyol, D. Life Cycle Analysis of Anaerobic Digestion of Wastewater Treatment Plants. In *Life Cycle Assessment of Wastewater Treatment*; Taylor & Francis: Oxfordshire, UK, 2018; p. 13.
14. Hameed, B.B.; Ismail, Z.Z. Decolorization, biodegradation and detoxification of reactive red azo dye using non-adapted immobilized mixed cells. *Biochem. Eng. J.* **2018**, *137*, 71–77. [\[CrossRef\]](#)
15. Yesilada, O.; Birhanli, E.; Geckil, H. Bioremediation and Decolorization of Textile Dyes by White Rot Fungi and Laccase Enzymes. In *Mycoremediation and Environmental Sustainability*; Springer: Cham, Switzerland, 2018; pp. 121–153.
16. Huang, X.; Sun, S.; Gao, B.; Yue, Q.; Wang, Y.; Li, Q. Coagulation behavior and floc properties of compound bioflocculant–polyaluminum chloride dual-coagulants and polymeric aluminum in low temperature surface water treatment. *J. Environ. Sci.* **2015**, *30*, 215–222. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Thakur, S.S.; Choubey, S. Use of Tannin based natural coagulants for water treatment: An alternative to inorganic chemicals. *Int. J. ChemTech Res.* **2014**, *6*, 3628–3634.
18. Mishra, A.; Bajpai, M. Flocculation behaviour of model textile wastewater treated with a food grade polysaccharide. *J. Hazard. Mater.* **2015**, *118*, 213–217. [\[CrossRef\]](#)
19. Lee, C.S.; Robinson, J.; Chong, M.F. A review on application of flocculants in wastewater treatment. *Process Saf. Environ. Prot.* **2014**, *92*, 489–508. [\[CrossRef\]](#)
20. Mishra, A.; Srinivasan, R.; Bajpai, M.; Dubey, R. Use of polyacrylamide-grafted Plantago psyllium mucilage as a flocculant for treatment of textile wastewater. *Colloid Polym. Sci.* **2004**, *282*, 722–727. [\[CrossRef\]](#)
21. Anasatakis, K.; Kalderis, D.; Diamadopoulos, E. Flocculation behavior of mallow and okra mucilage in treating wastewater. *Desalination* **2009**, *249*, 786–791. [\[CrossRef\]](#)
22. Rakhshaei, R.; Panahandeh, M. Stabilization of a magnetic nano-adsorbent by extracted pectin to remove methylene blue from aqueous solution: A comparative studying between two kinds of cross-linked pectin. *J. Hazard. Mater.* **2011**, *189*, 158–166. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Junior, O.M.C.; Barros, M.A.S.D.; Pereira, N.C. Study on coagulation and flocculation for treating effluents of textile industry. *Acta Sci. Technol.* **2012**, *35*, 83–88. [\[CrossRef\]](#)
24. Elieh-Ali-Komi, D.; Hamblin, M.R. Chitin and chitosan: Production and application of versatile biomedical nanomaterials. *Int. J. Adv. Res.* **2016**, *4*, 411.
25. Das, M.; Adholeya, A. Potential Uses of immobilized bacteria, fungi, algae, and their aggregates for treatment of organic and inorganic pollutants in wastewater. *Water Chall. Solut. Glob. Scale* **2015**, *1206*, 319–337. [\[CrossRef\]](#)
26. Jia, H.; Yuan, Q. Removal of nitrogen from wastewater using microalgae and microalgae–bacteria consortia. *Cogent Environ. Sci.* **2016**, *2*, 1275089. [\[CrossRef\]](#)
27. Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* **2001**, *77*, 247–255. [\[CrossRef\]](#)
28. Sen, G.; Ghosh, S.; Jha, U.; Pal, S. Hydrolyzed polyacrylamide grafted carboxymethylstarch (Hyd. CMS-g-PAM): An efficient flocculant for the treatment of textile industry wastewater. *Chem. Eng. J.* **2011**, *171*, 495–501. [\[CrossRef\]](#)
29. Chong, M.F. Direct flocculation process for wastewater treatment. In *Advance in Water Treatment and Pollution Prevention*; Springer: Dordrecht, The Netherlands, 2012.
30. Kudaibergenov, S.; Koetz, J.; Nuraje, N. Nanostructured hydrophobic polyampholytes: Self-assembly, stimuli-sensitivity, and application. *Adv. Compos. Hybrid Mater.* **2018**, *1*, 649–684. [\[CrossRef\]](#)
31. Markies, P.R.; Moonen, J.P.; Colin, P.O.; Evers, R.W.; Van Den Beucken, F.J.; Peng, K.U.S. Aqueous Inkjet Priming Composition Providing Both Pinning and Ink Spreading Functionality. Patent Application No. 15/938,893, 28 March 2018.
32. Hunger, K. *Industrial Dyes: Chemistry, Properties, Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2003.

33. Ghaly, A.E.; Ananthashankar, R.; Alhattab, M.V.V.R.; Ramakrishnan, V.V. Production, characterization and treatment of textile effluents: A critical review. *J. Chem. Eng. Process Technol.* **2014**, *5*, 1–19.
34. Yaseen, D.A.; Scholz, M. Textile dye wastewater characteristics and constituents of synthetic effluents: A critical review. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 1193–1226. [\[CrossRef\]](#)
35. Mishra, P.; Soni, R. Analysis of Dyeing and Printing Wastewater of Balotara Textile Industries. *Int. J. Chem. Sci.* **2016**, *14*, 1929–1938.
36. Liang, J.; Ning, X.A.; Kong, M.; Liu, D.; Wang, G.; Cai, H.; Sun, J.; Zhang, Y.; Lu, Z.; Yuan, Y. Elimination and ecotoxicity evaluation of phthalic acid esters from textile-dyeing wastewater. *Environ. Pollut.* **2017**, *231 Pt 1*, 115–122. [\[CrossRef\]](#)
37. Rawat, D.; Mishra, V.; Sharma, R.S. Detoxification of azo dyes in the context of environmental processes. *Chemosphere* **2016**, *155*, 591–605. [\[CrossRef\]](#)
38. Amini, M.; Arami, M.; Mahmoodi, N.M.; Akbari, A. Dye removal from colored textile wastewater using acrylic grafted nanomembrane. *Desalination* **2011**, *267*, 107–113. [\[CrossRef\]](#)
39. *Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders*; MDS Publishers Sdn. Bhd.: Kuala Lumpur, Malaysia, 2012.
40. Al-Daghistani, H. Bio-Remediation of Cu, Ni and Cr from rotogravure wastewater using immobilized, dead, and live biomass of indigenous thermophilic *Bacillus* species. *Internet J. Microbiol.* **2012**, *10*, 1–10.
41. Dey, S.; Islam, A. A review on textile wastewater characterization in Bangladesh. *Resour. Environ.* **2015**, *5*, 15–44.
42. FEPA. *Guidelines and Standards of Environmental Pollution Control in Nigeria*; Federal Environmental Protection Agency: Lagos, Nigeria, 1991.
43. Tortajada, C.; Joshi, Y.K. Water quality management in Singapore: The role of institutions, laws and regulations. *Hydrol. Sci. J.* **2014**, *59*, 1763–1774. [\[CrossRef\]](#)
44. United State Environmental Protection Agency. *Guidelines for Water Reuse*; US EPA: Washington, DC, USA, 2004.
45. Babel, S.; Kurniawan, T.A. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.* **2003**, *97*, 219–243. [\[CrossRef\]](#)
46. Shen, Y.; Yang, R.; Liao, Y.; Ma, J.; Mao, H.; Zhao, S. Tannin modified aminated silica as effective absorbents for removal of light rare earth ions in aqueous solution. *Desalin. Water Treat.* **2016**, *57*, 18529–18536. [\[CrossRef\]](#)
47. Akter, N.; Hossain, M.A.; Hassan, M.J.; Amin, M.K.; Elias, M.; Rahman, M.M.; Asiri, A.M.; Siddiquey, I.A.; Hasnat, M.A. Amine modified tannin gel for adsorptive removal of Brilliant Green dye. *J. Environ. Chem. Eng.* **2016**, *4*, 1231–1241. [\[CrossRef\]](#)
48. Ho, Y.C.; Norli, I.; Abbas, F.M.A.; Morad, N. Enhanced turbidity removal in water treatment by using emerging vegetal biopolymer composite: A characterization and optimization study. *Desalin. Water Treat.* **2016**, *57*, 1779–1789. [\[CrossRef\]](#)
49. Bongiovani, M.C.; Camacho, F.P.; Coldebella, P.F.; Valverde, K.C.; Nishi, L.; Bergamasco, R. Removal of natural organic matter and trihalomethane minimization by coagulation/flocculation/filtration using a natural tannin. *Desalin. Water Treat.* **2016**, *57*, 5406–5415. [\[CrossRef\]](#)
50. Jung, Y.; Kwon, M.; Kye, H.; Abrha, Y.W.; Kang, J.W. Evaluation of Moringa oleifera seed extract by extraction time: Effect on coagulation efficiency and extract characteristic. *J. Water Health* **2018**, *16*, 904–913. [\[CrossRef\]](#)
51. Salehizadeh, H.; Yan, N.; Farnood, R. Recent advances in polysaccharide bio-based flocculants. *Biotechnol. Adv.* **2018**, *36*, 92–119. [\[CrossRef\]](#)
52. Arunkumar, P.; Sadish Kumar, V.; Saran, S.; Bindun, H.; Devipriya, S.P. Isolation of active coagulant protein from the seeds of *Strychnos potatorum*—a potential water treatment agent. *Environ. Technol.* **2018**, *40*, 1624–1632. [\[CrossRef\]](#)
53. Roy, U.; Sengupta, S.; Banerjee, P.; Das, P.; Bhowal, A.; Datta, S. Assessment on the decolourization of textile dye (Reactive Yellow) using *Pseudomonas* sp. immobilized on fly ash: Response surface methodology optimization and toxicity evaluation. *J. Environ. Manag.* **2018**, *223*, 185–195. [\[CrossRef\]](#)
54. Mathur, M.; Gola, D.; Panja, R.; Malik, A.; Ahammad, S.Z. Performance evaluation of two *Aspergillus* spp. for the decolourization of reactive dyes by bioaccumulation and biosorption. *Environ. Sci. Pollut. Res.* **2018**, *25*, 345–352. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Jeyaseelan, K.; Murugesan, A.; Palanisamy, S.B. Biopolymer Technologies for Environmental Applications. In *Nanoscience and Biotechnology for Environmental Applications*; Springer: Cham, Switzerland, 2019; pp. 55–83.
56. Gunatilake, S.K. Methods of removing heavy metals from industrial wastewater. *Methods* **2015**, *1*, 14.

57. Du, Q.; Wei, H.; Li, A.M. Multi-functional natural polymer based water treatment agents. *Environ. Chem.* **2018**, *37*, 1293–1310.
58. Aisyah, S.I.; Norfariha, M.S.; Azlan, M.A.; Norli, I. Comparison of Synthetic and Natural Organic Polymers as Flocculant for Textile Wastewater Treatment. *Iran. J. Energy Environ.* **2014**, *5*, 436–445.
59. Onukwuli, O.D.; Obiora-Okafo, I.A.; Omotoma, M. Characterization and Colour Removal from An Aqueous Solution Using Bio-Coagulants: Response Surface Methodological Approach. *J. Chem. Technol. Metall.* **2019**, *54*, 77–89.
60. Jagaba, A.H.; Abubakar, S.; Lawal, I.M.; Latiff, A.A.A.; Umaru, I. Wastewater Treatment Using Alum, the Combinations of Alum-Ferric Chloride, Alum-Chitosan, Alum-Zeolite and Alum-Moringa Oleifera as Adsorbent and Coagulant. *Int. J. Eng. Manag.* **2018**, *2*, 67–75. [[CrossRef](#)]
61. Janaki, V.; Vijayaraghavan, K.; Oh, B.T.; Ramasamy, A.K.; Kamala-Kannan, S. Synthesis, characterization and application of cellulose/polyaniline nanocomposite for the treatment of simulated textile effluent. *Cellulose* **2013**, *20*, 1153–1166. [[CrossRef](#)]
62. Vijayaraghavan, G.; Kumar, P.V.; Chandrakanthan, K.; Selvakumar, S. Acanthocereus tetragonus an effective natural coagulant for decolorization of synthetic dye wastewater. *J. Mater. Environ. Sci.* **2017**, *8*, 3028–3033.
63. Agbahoungbata, M.Y.; Fatombi, J.K.; Ayedoun, M.A.; Idohou, E.; Sagbo, E.V.; Osseni, S.A.; Aminou, T. Removal of reactive dyes from their aqueous solutions using Moringa oleifera seeds and Grewia venusta peel. *Desalin. Water Treat.* **2016**, *57*, 22609–22617. [[CrossRef](#)]
64. Freitas, T.K.F.S.; Oliveira, V.M.; De Souza, M.T.F.; Geraldino, H.C.L.; Almeida, V.C.; Fávaro, S.L.; Garcia, J.C. Optimization of coagulation-flocculation process for treatment of industrial textile wastewater using okra (A. esculentus) mucilage as natural coagulant. *Ind. Crops Prod.* **2015**, *76*, 538–544. [[CrossRef](#)]
65. Naseeruteen, F.; Hamid, N.S.A.; Suah, F.B.M.; Ngah, W.S.W.; Mehamod, F.S. Adsorption of malachite green from aqueous solution by using novel chitosan ionic liquid beads. *Int. J. Biol. Macromol.* **2018**, *107*, 1270–1277. [[CrossRef](#)] [[PubMed](#)]
66. Aboulhassan, M.A.; Souabi, S.; Yaacoubi, A.; Baudu, M. Coagulation efficacy of a tannin coagulant agent compared to metal salts for paint manufacturing wastewater treatment. *Desalin. Water Treat.* **2016**, *57*, 19199–19205. [[CrossRef](#)]
67. Sanghi, R.; Bhattacharya, B.; Singh, V. Use of Cassia javahikai seed gum and gum-g-polyacrylamide as coagulant aid for the decolorization of textile dye solutions. *Bioresour. Technol.* **2006**, *97*, 1259–1264. [[CrossRef](#)]
68. Wu, H.; Yang, R.; Li, R.; Long, C.; Yang, H.; Li, A. Modeling and optimization of the flocculation processes for removal of cationic and anionic dyes from water by an amphoteric grafting chitosan-based flocculant using response surface methodology. *Environ. Sci. Pollut. Res.* **2015**, *22*, 13038–13048. [[CrossRef](#)]
69. Lin, Q.; Gao, M.; Chang, J.; Ma, H. Adsorption properties of crosslinking carboxymethyl cellulose grafting dimethyldiallylammonium chloride for cationic and anionic dyes. *Carbohydr. Polym.* **2016**, *151*, 283–294. [[CrossRef](#)]
70. Du, S.; Wang, L.; Xue, N.; Pei, M.; Sui, W.; Guo, W. Polyethyleneimine modified bentonite for the adsorption of amino black 10B. *J. Solid State Chem.* **2017**, *252*, 152–157. [[CrossRef](#)]
71. Liu, M.; Chen, Q.; Lu, K.; Huang, W.; Lü, Z.; Zhou, C.; Gao, C. High efficient removal of dyes from aqueous solution through nanofiltration using diethanolamine-modified polyamide thin-film composite membrane. *Sep. Purif. Technol.* **2017**, *173*, 135–143. [[CrossRef](#)]
72. Rocher, V.; Siaugue, J.M.; Cabuil, V.; Bee, A. Removal of organic dyes by magnetic alginate beads. *Water Res.* **2008**, *42*, 1290–1298. [[CrossRef](#)]
73. Yu, B.; Yang, B.; Li, G.; Cong, H. Preparation of monodisperse cross-linked poly (glycidyl methacrylate)-Fe₃O₄-diazoresin magnetic microspheres with dye removal property. *J. Mater. Sci.* **2017**, *53*, 6471–6481. [[CrossRef](#)]
74. Zeng, L.; Xiao, L.; Long, Y.; Shi, X. Trichloroacetic acid-modulated synthesis of polyoxometalate@ UiO-66 for selective adsorption of cationic dyes. *J. Colloid Interface Sci.* **2018**, *516*, 274–283. [[CrossRef](#)]
75. Shao, H.; Qi, Y.; Liang, S.; Qin, S.; Yu, J. Polypropylene composite hollow fiber ultrafiltration membranes with an acrylic hydrogel surface by in situ ultrasonic wave-assisted polymerization for dye removal. *J. Appl. Polym. Sci.* **2019**, *136*, 47099. [[CrossRef](#)]
76. Buthelezi, S.P.; Olaniran, A.O.; Pillay, B. Textile dye removal from wastewater effluents using bioflocculants produced by indigenous bacterial isolates. *Molecules* **2012**, *17*, 14260–14274. [[CrossRef](#)]
77. Pearce, C.I.; Lloyd, J.R.; Guthrie, J.T. The removal of colour from textile wastewater using whole bacterial cells: A review. *Dye. Pigment.* **2003**, *58*, 179–196. [[CrossRef](#)]

78. Kurade, M.B.; Waghmode, T.R.; Xiong, J.Q.; Govindwar, S.P.; Jeon, B.H. Decolorization of textile industry effluent using immobilized consortium cells in upflow fixed bed reactor. *J. Clean. Prod.* **2019**, *213*, 884–891. [\[CrossRef\]](#)
79. Chanwala, J.; Kaushik, G.; Dar, M.A.; Upadhyay, S.; Agrawal, A. Process optimization and enhanced decolorization of textile effluent by *Planococcus* sp. isolated from textile sludge. *Environ. Technol. Innov.* **2019**, *13*, 122–129. [\[CrossRef\]](#)
80. Aziz, H.A.; Rahim, N.A.; Ramli, S.F.; Alazaiza, M.Y.; Omar, F.M.; Hung, Y.T. Potential use of *Dimocarpus longan* seeds as a flocculant in landfill leachate treatment. *Water* **2018**, *10*, 1672. [\[CrossRef\]](#)
81. León, O.; Muñoz-Bonilla, A.; Soto, D.; Pérez, D.; Rangel, M.; Colina, M.; Fernández-García, M. Removal of anionic and cationic dyes with bioadsorbent oxidized chitosans. *Carbohydr. Polym.* **2018**, *194*, 375–383. [\[CrossRef\]](#)
82. Borthakur, P.; Boruah, P.K.; Hussain, N.; Sharma, B.; Das, M.R.; Matić, S.; Minofar, B. Experimental and molecular dynamics simulation study of specific ion effect on the graphene oxide surface and investigation of the influence on reactive extraction of model dye molecule at water–organic interface. *J. Phys. Chem. C* **2016**, *120*, 14088–14100. [\[CrossRef\]](#)
83. Das, R.; Ghorai, S.; Pal, S. Flocculation characteristics of polyacrylamide grafted hydroxypropyl methyl cellulose: An efficient biodegradable flocculant. *Chem. Eng. J.* **2013**, *229*, 144–152. [\[CrossRef\]](#)
84. Rahangdale, D.; Kumar, A. Derivatized Chitosan: Fundamentals to Applications. In *Biopolymer Grafting*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 251–284.
85. Abiola, O.N. Polymers for Coagulation and Flocculation in Water Treatment. In *Polymeric Materials for Clean Water*; Springer: Cham, Switzerland, 2019; pp. 77–92.
86. Patel, H.; Vashi, R.T. Removal of Congo Red dye from its aqueous solution using natural coagulants. *J. Saudi Chem. Soc.* **2012**, *16*, 131–136. [\[CrossRef\]](#)
87. Liaquat, L.; Sadiq, S.; Batool, Z.; Tabassum, S.; Shahzad, S.; Afzal, A.; Haider, S. Acute aluminum chloride toxicity revisited: Study on DNA damage and histopathological, biochemical and neurochemical alterations in rat brain. *Life Sci.* **2019**, *217*, 202–211. [\[CrossRef\]](#) [\[PubMed\]](#)
88. Lourenço, A.D.S. Development of Novel Flocculants to Treat Oily Waters Using Health-Friendly Processes. Ph.D. Thesis, Universidade de Coimbra, Coimbra, Portugal, 2018.
89. Li, H.; Hu, C.; Yu, H.; Chen, C. Chitosan composite scaffolds for articular cartilage defect repair: A review. *RSC Adv.* **2018**, *8*, 3736–3749. [\[CrossRef\]](#)
90. Crini, G.; Lichtfouse, E.; Wilson, L.D.; Morin-Crini, N. Conventional and non-conventional adsorbents for wastewater treatment. *Environ. Chem. Lett.* **2018**, *17*, 195–213. [\[CrossRef\]](#)
91. Wilts, E.M.; Herzberger, J.; Long, T.E. Addressing water scarcity: Cationic polyelectrolytes in water treatment and purification. *Polym. Int.* **2018**, *67*, 799–814. [\[CrossRef\]](#)
92. Grenda, K.; Arnold, J.; Hunkeler, D.; Gamelas, J.A.F.; Rasteiro, M.G. Tannin-based coagulants from laboratory to pilot plant scales for coloured wastewater treatment. *BioResources* **2018**, *13*, 2727–2747. [\[CrossRef\]](#)
93. Dotto, J.; Fagundes-Klen, M.R.; Veit, M.T.; Palácio, S.M.; Bergamasco, R. Performance of different coagulants in the coagulation/flocculation process of textile wastewater. *J. Clean. Prod.* **2019**, *208*, 656–665. [\[CrossRef\]](#)
94. Freitas, T.F.K.S.; Almeida, C.A.; Manholer, D.D.; Geraldino, H.C.L.; de Souza, M.T.F.; Garcia, J.C. Review of utilization plant-based coagulants as alternatives to textile wastewater treatment. In *Detox Fashion*; Springer: Singapore, 2018; pp. 27–79.
95. Benalia, A.; Derbal, K.; Panico, A.; Pirozzi, F. Use of Acorn Leaves as a Natural Coagulant in a Drinking Water Treatment Plant. *Water* **2019**, *11*, 57. [\[CrossRef\]](#)
96. Mhaisalkar, V.A.; Paramasivam, R.; Bhole, A.G. Optimizing physical parameters of rapid mix design for coagulation-flocculation of turbid waters. *Water Res.* **1991**, *25*, 43–52. [\[CrossRef\]](#)
97. Yukselen, M.A.; Gregory, J. The effect of rapid mixing on the break-up and re-formation of flocs. *Environ. Clean Technol.* **2004**, *79*, 782–788. [\[CrossRef\]](#)
98. Ahmed, S.; Ayoub, G.; Al-Hindi, M.; Azizi, F. The effect of fast mixing conditions on the coagulation–flocculation process of highly turbid suspensions using liquid bittern coagulant. *Desalin. Water Treat.* **2015**, *53*, 3388–3396.
99. Ramphal, S.; Sibiya, S.M. Optimization of time requirement for rapid mixing during coagulation using a photometric dispersion analyzer. *Procedia Eng.* **2014**, *70*, 1401–1410. [\[CrossRef\]](#)

100. Zhang, Z.; Liu, D.; Hu, D.; Li, D.; Ren, X.; Cheng, Y.; Luan, Z. Effects of Slow-Mixing on the Coagulation Performance of Polyaluminum Chloride (PACl). *Chin. J. Chem. Eng.* **2013**, *21*, 318–323. [[CrossRef](#)]
101. Bernard, K.N.M.; Sylvere, N.K.; Patrice, K.G.; Joseph, K.G. Coagulation and Sedimentation of Concentrated Laterite Suspensions: Comparison of Hydrolyzing Salts in Presence of *Grewia* spp. *Biopolymer. J. Chem.* **2019**, *2019*, 1–9.
102. Hamza, M.F.; Wei, Y.; Mira, H.I.; Adel, A.H.; Guibal, E. Synthesis and adsorption characteristics of grafted hydrazinyl amine magnetite-chitosan for Ni (II) and Pb (II) recovery. *Chem. Eng. J.* **2019**, *362*, 310–324. [[CrossRef](#)]
103. Yang, J.; Li, M.; Wang, Y.; Wu, H.; Zhen, T.; Xiong, L.; Sun, Q. Double cross-linked chitosan composite films developed with oxidized tannic acid and ferric ions exhibit high strength and excellent water resistance. *Biomacromolecules* **2019**, *20*, 801–812. [[CrossRef](#)]
104. Ranote, S.; Kumar, D.; Kumari, S.; Kumar, R.; Chauhan, G.S.; Joshi, V. Green synthesis of Moringa oleifera gum-based bifunctional polyurethane foam braced with ash for rapid and efficient dye removal. *Chem. Eng. J.* **2019**, *361*, 1586–1596. [[CrossRef](#)]
105. Tian, H.; Fan, H.; Ma, J.; Liu, Z.; Ma, L.; Lei, S.; Long, C. Pt-decorated zinc oxide nanorod arrays with graphitic carbon nitride nanosheets for highly efficient dual-functional gas sensing. *J. Hazard. Mater.* **2018**, *341*, 102–111. [[CrossRef](#)] [[PubMed](#)]
106. Shan, C.; Wang, L.; Li, Z.; Zhong, X.; Hou, Y.; Zhang, L.; Shi, F. Graphene oxide enhanced polyacrylamide-alginate aerogels catalysts. *Carbohydr. Polym.* **2019**, *203*, 19–25. [[CrossRef](#)]
107. Borazan, A.A.; Acikgoz, C. Effect of Quince Variety on The Quality Of Pectin: Chemical Composition And Characterization. *Int. J. Pharm. Chem. Biol. Sci.* **2017**, *7*, 393–400.
108. Sirajo, A.Z.; Vishalakshi, B. Microwave assisted synthesis of poly (diallyldimethylammonium chloride) grafted locust bean gum: Swelling and dye adsorption studies. *Indian J. Adv. Chem. Sci. S* **2016**, *1*, 88–91.
109. Zahrim, A.Y.; Tizaoui, C.; Hilal, N. Evaluation of several commercial synthetic polymers as flocculant aids for removal of highly concentrated CI Acid Black 210 dye. *J. Hazard. Mater.* **2010**, *182*, 624–630. [[CrossRef](#)] [[PubMed](#)]
110. Wolf, G.; Schneider, R.M.; Bongiovani, M.C.; Morgan Uliana, E.; Garcia Do Amaral, A. Application of coagulation/flocculation process of dairy wastewater from conventional treatment using natural coagulant for reuse. *Chem. Eng. Trans.* **2015**, *43*, 2041–2046. [[CrossRef](#)]
111. Ho, Y.C.; Norli, I.; Alkarkhi, A.F.; Morad, N. New vegetal biopolymeric flocculant: A degradation and flocculation study. *Iran. J. Energy Environ.* **2014**, *5*, 2–3. [[CrossRef](#)]
112. Razali, M.A.A.; Ahmad, Z.; Ariffin, A. Treatment of pulp and paper mill wastewater with various molecular weight of PolyDADMAC induced flocculation with polyacrylamide in the hybrid system. *Adv. Chem. Eng. Sci.* **2012**, *2*, 490. [[CrossRef](#)]
113. Graham, N.; Gang, F.; Fowler, G.; Watts, M. Characterisation and coagulation performance of a tannin-based cationic polymer: A preliminary assessment. *Colloids Surf. A Physicochem. Eng. Asp.* **2008**, *327*, 9–16. [[CrossRef](#)]
114. De Assis, L.K.; Damasceno, B.S.; Carvalho, M.N.; Oliveira, E.H.; Ghislandi, M.G. Adsorption capacity comparison between graphene oxide and graphene nanoplatelets for the removal of colored textile dyes from wastewater. *Environ. Technol.* **2019**, *41*, 2360–2371. [[CrossRef](#)]
115. Zhao, H.Z.; Sun, Y.; Xu, L.N.; Ni, J.R. Removal of Acid Orange 7 in simulated wastewater using a three-dimensional electrode reactor: Removal mechanisms and dye degradation pathway. *Chemosphere* **2010**, *78*, 46–51. [[CrossRef](#)]
116. Torres, M.A.; Vieira, R.S.; Beppu, M.M.; Arruda, E.J.; Santana, C.C. Production of chemically modified chitosan microspheres by a spraying and coagulation method. *Mater. Res.* **2007**, *10*, 347–352. [[CrossRef](#)]
117. Costine, A.; Cox, J.; Travaglini, S.; Lubansky, A.; Fawell, P.; Misslitz, H. Variations in the molecular weight response of anionic polyacrylamides under different flocculation conditions. *Chem. Eng. Sci.* **2018**, *176*, 127–138. [[CrossRef](#)]
118. Guo, K.; Gao, B.; Wang, W.; Yue, Q.; Xu, X. Evaluation of molecular weight, chain architectures and charge densities of various lignin-based flocculants for dye wastewater treatment. *Chemosphere* **2019**, *215*, 214–226. [[CrossRef](#)]

119. Liang, G.; Nguyen, A.V.; Chen, W.; Nguyen, T.A.; Biggs, S. Interaction forces between goethite and polymeric flocculants and their effect on the flocculation of fine goethite particles. *Chem. Eng. J.* **2018**, *334*, 1034–1045. [[CrossRef](#)]
120. Wang, S.; Kong, F.; Fatehi, P.; Hou, Q. Cationic High Molecular Weight Lignin Polymer: A Flocculant for the Removal of Anionic Azo-Dyes from Simulated Wastewater. *Molecules* **2018**, *23*, 2005. [[CrossRef](#)] [[PubMed](#)]
121. Qiu, J.; Wang, H.; Du, Z.; Cheng, X.; Liu, Y.; Wang, H. Preparation of polyacrylamide via dispersion polymerization with gelatin as a stabilizer and its synergistic effect on organic dye flocculation. *J. Appl. Polym. Sci.* **2018**, *135*, 46298. [[CrossRef](#)]
122. Zhao, C.; Zheng, H.; Sun, Y.; Zhang, S.; Liang, J.; Liu, Y.; An, Y. Evaluation of a novel dextran-based flocculant on treatment of dye wastewater: Effect of kaolin particles. *Sci. Total Environ.* **2018**, *640*, 243–254. [[CrossRef](#)] [[PubMed](#)]
123. Bolto, B.; Gregory, J. Organic polyelectrolytes in water treatment. *Water Res.* **2007**, *41*, 2301–2324. [[CrossRef](#)]
124. Ghosh, S.; Sen, G.; Jha, U.; Pal, S. Novel Biodegradable Polymeric Flocculant Based on Polyacrylamide-grafted Tamarind Kernel Polysaccharide. *Bioresour. Technol.* **2011**, *101*, 9638–9644. [[CrossRef](#)]
125. Wang, W.; Chen, Z.; Wu, K.; Liu, Z.; Yang, S.; Yang, Q.; Dzakpasu, M. Coagulation performance of cucurbit [8] uril for the removal of azo dyes: Effect of solution chemistry and coagulant dose. *Water Sci. Technol.* **2018**, *78*, 415–423. [[CrossRef](#)] [[PubMed](#)]
126. Wen, Y.; Zheng, W.; Yang, Y.; Cao, A.; Zhou, Q. Influence of Al³⁺ addition on the flocculation and sedimentation of activated sludge: Comparison of single and multiple dosing patterns. *Water Res.* **2015**, *75*, 201–209. [[CrossRef](#)] [[PubMed](#)]
127. Wu, H.; Liu, Z.; Yang, H.; Li, A. Evaluation of chain architectures and charge properties of various starch-based flocculants for flocculation of humic acid from water. *Water Res.* **2016**, *96*, 126–135. [[CrossRef](#)]
128. Lugo, L.; Martín, A.; Diaz, J.; Pérez-Flórez, A.; Celis, C. Implementation of Modified *Acacia* Tannin by Mannich Reaction for Removal of Heavy Metals (Cu, Cr and Hg). *Water* **2020**, *12*, 352. [[CrossRef](#)]
129. Razzaz, A.; Ghorban, S.; Hosayni, L.; Irani, M.; Aliabadi, M. Chitosan nanofibers functionalized by TiO₂ nanoparticles for the removal of heavy metal ions. *J. Taiwan Inst. Chem. Eng.* **2016**, *58*, 333–343. [[CrossRef](#)]
130. Momeni, M.M.; Kahforoushan, D.; Abbasi, F.; Ghanbarian, S. Using Chitosan/CHPATC as coagulant to remove color and turbidity of industrial wastewater: Optimization through RSM design. *J. Environ. Manag.* **2018**, *211*, 347–355. [[CrossRef](#)]
131. Sán Beltrán-Heredia, J.; Sánchez-Martín, J.; Martín-García, L. Multiparameter quantitative optimization in the synthesis of a novel coagulant derived from tannin extracts for water treatment. *Water Air Soil Pollut.* **2012**, *223*, 2277–2286. [[CrossRef](#)]
132. Yang, Z.; Yang, H.; Jiang, Z.; Cai, T.; Li, H.; Cheng, R. Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethyl chitosan-graft-polyacrylamide. *J. Hazard. Mater.* **2013**, *254*, 36–45. [[CrossRef](#)]
133. He, K.; Lou, T.; Wang, X.; Zhao, W. Preparation of lignosulfonate–acrylamide–chitosan ternary graft copolymer and its flocculation performance. *Int. J. Biol. Macromol.* **2015**, *81*, 1053–1058. [[CrossRef](#)]
134. Feira, J.M.C.D.; Klein, J.M.; Forte, M.M.D.C. Ultrasound-assisted synthesis of polyacrylamide-grafted sodium alginate and its application in dye removal. *Polímeros* **2018**, *28*, 139–146. [[CrossRef](#)]
135. Lou, T.; Wang, X.; Song, G.; Cui, G. Synthesis and flocculation performance of a chitosan-acrylamide-fulvic acid ternary copolymer. *Carbohydr. Polym.* **2017**, *170*, 182–189. [[CrossRef](#)]
136. Zhang, L.W.; Hua, J.R.; Zhu, W.J.; Liu, L.; Du, X.L.; Meng, R.J.; Yao, J.M. Flocculation performance of hyperbranched polyethylenimine-grafted cellulose in wastewater treatment. *ACS Sustain. Chem. Eng.* **2018**, *6*, 1592–1601. [[CrossRef](#)]
137. Cai, T.; Li, H.; Yang, R.; Wang, Y.; Li, R.; Yang, H.; Cheng, R. Efficient flocculation of an anionic dye from aqueous solutions using a cellulose-based flocculant. *Cellulose* **2015**, *22*, 1439–1449. [[CrossRef](#)]
138. Zhou, L.; Zhou, H.; Yang, X. Preparation and performance of a novel starch-based inorganic/organic composite coagulant for textile wastewater treatment. *Sep. Purif. Technol.* **2019**, *210*, 93–99. [[CrossRef](#)]
139. Beltrán-Heredia, J.; Sánchez-Martín, J.; Gómez-Muñoz, M.C. New coagulant agents from tannin extracts: Preliminary optimisation studies. *Chem. Eng. J.* **2010**, *162*, 1019–1025. [[CrossRef](#)]

140. Sánchez-Martín, J.; Beltrán-Heredia, J.; Solera-Hernández, C. Surface water and wastewater treatment using a new tannin-based coagulant. Pilot plant trials. *J. Environ. Manag.* **2010**, *91*, 2051–2058. [[CrossRef](#)]
141. Peng, Z.; Zhong, H. Adsorption of heavy metal ions from aqueous solution by tannin-based hydrogel. *Asian J. Chem.* **2014**, *26*, 3605–3608. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).