Polymers in Wastewater Treatment

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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.

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, 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.

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 nonbiodegradable compounds [2]. 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 [3]. Natural coagulants are of great interest to scientists, since they are natural, low-cost products, characterized by their environmentally friendly behavior, and are presumed to be safe for human health [4]. 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) [5][6].

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 [7]. 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 [8][9][10][11][12][13][14]. 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 [15]. The physical modification process includes the blending of two or more types of the polymer at 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.

2. 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 [16]. 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 [17], or synthesized, such as acrylamide based poly-(2-methacryloyloxyethyl)-trimethylammonium chloride [18][19][20]. 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 [21][22][23][24][25]. 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 [26]. 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 [27]. Moreover, renewable resources are abundant, and the aspect of biodegradability attracts many researchers [28]. The studies concerning the application of natural polymers in water and wastewater treatment are listed in Table 1.

Table 1. 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%	[29]
	Synthetic dye	Adsorption	pectin dose 20 mg; pH 8 20 mg/l of Methylene blue	Methylene blue dye	45.00%	[30]
	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%	[31]
	Synthetic dye	Adsorption	no pH adjustment; 20 mg of beads were added to 50	Methylene blue dye	1550.3 mg/g for Pectin bead and 2307.9 mg/g for	[32]

			mL of the dye solution		pectin/cellulose microfiber bead	
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%	[33]
	Synthetic dye	Adsorption	chitosan beads, 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium (pH 4.0, a 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	[34]
	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%	[32]
Cellulose/Polyaniline (Ce/Pn)	Synthetic dye	Adsorption process		Remazol dye	95.90%, 91.90%,	[33]

Nanocomposite				effluent	92.70%, and 95.70% of RBBR, RO, RV, and RBK, respectively.	
Alginate	Synthetic dyes	Activated carbon		Methylene blue and Methyl orange dyes	50.00% Methylene blue in 10 min and Methyl orange in 17 min	[34]
Acanthocerous 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%	[34]
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	[35]
GrewiaVenusta 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	[35]
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 Fe^{3+}	-	93.57% 5.78 mg g−1	[36]

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 Duasyn direct dye Acid black 2	> 90.00% 89.00% 99.00% 83.00%	[37]
	Manufacturing wastewater treatment	Coagulation and flocculation	-	-	99.00%	[37]
Gums C. Javahikai Seed Gum (Cj)	Synthetic dyes	Coagulation and flocculation		Direct dyes	>70.00%	[38]

3. Conclusion

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.

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