ISBN: 978-81-19149-97-1

17. Green Polysaccharide Material for the Removal of Color, TDS, COD and Chloride from Dyeing Effluent

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Abstract:

Textile industries are responsible for one of the major environmental pollution problems in the world because they release undesirable dye effluents. The majority of dyeing enterprises either treat their effluents completely or only partially before releasing them into the environment. The ecosystem and human health may be at risk due to the discharge of these dye effluents and the structure of the persistent dye, which has hazardous qualities.

In the present investigation, the synthetic dye effluent was collected from the textile dyeing unit and the physic- chemical characteristics were analyzed using APHA standard method. The results stressed to treat the effluent by using eco-friendly green materials. Tamarindus indica L seed Polysaccharide was used for the removal of color, TDS, COD and Chloride from the black dye effluent.

The effluent was subjected to treatment with natural polysachharide dosage such as 0.1g, 0.2g, 0.3g, 0.4g, 0.5g isolated from Tamarindus indica L seed. About 81% of TDS, 77% of COD and 76% of Chloride removal were obtained at 0.5g of dosage treatment of polysachharide proved the ability of coagulation and pollutant removal capability.

The functional group changes in the natural coagulants and chemical sludge were analyzed before and after the treatment which were characterized by using the FTIR technique. The raw dye sample and treated dye sample were qualitatively analyzed by GCMS analytical method. Hence, the present study suggests that, the possibilities for the use of Tamarindus indica. L seed polysaccharides for the treatment of dye effluent.

Keywords:

polysachharide, natural coagulant, Tamarindus indica L, dyeing effluent, TDS, COD.

17.1 Introduction:

Water is valuable natural resources available on the blue planet of earth and plays a pivotal role in the purpose of irrigation, drinking, aquaculture and livestock usage [1]. According to the WHO organization, inadequate sanitation and pollution caused about 80% of all diseases in humans [2]. Water is polluted by natural and anthropogenic activities. Among the anthropogenic activities, industries are playing major role to pollute the environment. Industries are consuming more water and followed by producing more waste water. Textile industries are causing one of the major environmental pollution problems inthe world because they release undesirable dye effluents. Many dyeing unit enterprise, treat their effluent partially or fully before disposing them into the environment. The majority (93%) of the stream water resources usedas feed for the textile manufacturing for commerce and they turn into colored effluent, consisting various chemical compounds [3-4]. Manufacture of 1 kg of textile cloth uses roughly 0.15 m^3 of water, with a discharge of 3000 m^3 effluent for processing 20 tonnes of fabrics each day [5]. Dye effluent contains a variety of synthetic compounds as pollutants, each pollutant has shown diverse levelof toxicity and poses a different risk to environment and organisms. Almost all the compounds in the discharge stream have the potential to cause cancer and are not biodegradable [6]. The presence of dye molecules in the hydrosphere hinders the biological pursuit of aquatic life byreducing sunlight's ability to penetrate deeply into water bodies [7]. Animalresearch experiment revealed the dye ingestion has a variety of negative effects, including carcinogenic, genotoxic, mutagenic and teratogenic effects [8]). Many advanced treatment techniques are available, but they are high cost and cause secondary pollution problems like more solid waste generation. Hence, low cost, eco-friendly material, an alternative for synthetic coagulants are need of hour.

Phytocoagulants used for water treatment creates a lower volume of sludge with the treatment of various amount of effective coagulant dosage, retains the alkalinity as such, without any change during the treatment of waste, bio decomposable, safe for human, organisms and the environment [9]. Hence, a plant coagulant *Tamarindus indica* L has chosen for this study. Tamarind seed powder has polysachharide and efficient in reducing turbid from murky water. Many researchers have reported the presence of polysaccharides that might contribute to its high flocculatingactivity of tamarind seed. Hence, the present study is aimed to treat the textile dye effluent by environment-friendly treatment techniques using Natural coagulants Polysaccharides.

17.2 Materials and Methods:

17.2.1 Materials:

Required Tamarindus indica L. natural coagulants seed was purchased from Kodaikanal market and dyeing effluent was collected from typical dyeing unit located at Combatore.

17.2.2 Methods:

A. Characterization of Dyeing Effluent: The physical and chemical characteristics of dye effluent were analyzed using standard methods [10].

B. Process of Natural Coagulant- *Tamarindus indica* L. seeds: The seed was subjected to wash with normal water, and then rinsed by using sterilized deionized water and immersed in distilled water to overnight. Then, the seed was taken and dried in shadow to remove the outer shell, and crushed in order to make it powder. The fine particles of sample was sieved (25 BSS) and store up in a sealed container.

C. Isolation of Polysaccharide from *Tamarindus indica* L. seeds: Polysachharide was isolated as per method given by Nayak et al. (2015) [11]. The thin film of isolated polysachharide crushed and BSS -18 size was used for treatment of dye effluent.

Figure 1: Isolated polysachharide from *Tamarindus indica L seed*

D. Effect of *Tamarindus indica* L. Polysaccharide on the Removal of Colour, TDS, COD and Chloride from the Dye Effluent: Jar test- Flocculator was used to find the optimum dose of polysachharide for dye effluent treatment. It was carried out by using Jar test apparatus/Flocculator (Kemi make). Test was conducted by using 1g, 2g, 3g, 4g, 5g, 6g for 1000ml of effluent. An optimal dosage 0.5g/100ml (5g/1000ml) was found out. The control was maintained without adding any coagulants. The treated contents were filtered through filter paper (Whatman No.1) and analyzed the TDS, COD and colour parameters. The experiments were conducted in thrice.

Figure 2: Jar test for optimization of dosage

F. FTIR Characterization of the natural coagulants and treated sludge of dye effluent: *Tamarindus indica* L. polysaccharide was analyzed for FTIR to spot the functional chemical group available in the coagulants and after the treatment any changes made in the functional groups. The dried sludge powder obtained after the treatment was characterized by FT-IR (Model: Perkin Elmer Spectrum Frontier). The FT-IR spectrum was obtained in the mid-IR region of 450-4000cm-1. The spectrum was recorded using ATR (Attenuated Reflectance Technique). The active chemical groups are identified by comparing the peaks generated by the samplewith that of the reference standard.

G. GC-MS Analysis of the Before and After the Treatment of Dye Effluent: To identify the synthetic compounds, present in the raw effluent and Tamarindus polysaccharide treated dye effluent was subjected to Gas Chromatography-Mass Spectroscopy analysis. Gas Chromatography-Mass Spectroscopy (Agilent 7890B GC connected to 5977A MSD) analysis was performed. The reduction of the impurities was analyzed.

17.3 Result and Discussion:

17.3.1 Physicochemical Characteristics of Dyeing Effluent:

The physic chemical characteristics of dyeing effluent such as pH, Color, Odor, TDS, TSS, DO, COD, BOD, Chloride, Calcium, Nitrate, Phosphate, Sulphate, Alkalinity, Acidity, Chloride, Sulphate, Phosphate,and COD were analyzed and the result is depicted in the table 17.1.

The pH is an imperative parameter. The presence of pollutants alters the pH of the water. The sample showed alkaline pH of 8.91 due to the various salts sodium chloride, sodium hypochlorite, carbonates and bicarbonates used for coloring the products [12].

Temperature plays a vital role in the growth of all living organisms. It is an essential physiological parameter that manages aquatic organisms [13]. The dye effluent colour and odour were found to be green and unpleasant respectively. The coloured dye stuff toxic and potentially toxic and cause mutagenic effect to aquatic plants and fauna [14].

The temperature of the sample was found to be 37°C during discharge. Textile dyeing effluent contains higher amount of all kind of solids owed to the presence of a elevated level of dyestuff. The total solids level in the raw effluent was 8041mg/L. The higher solids may be the occurrence of dissolved state solids and floating solids [15] and reported that the textile dyeing effluent contains a higher level of Total solids [16].

The higher TDS values may be various salts used for the dyeing process [17]. Also, the higher values of TSS may be attributed to fibers from cloth and different dyestuffs used for the dyeing process [18]. The TSS affects the light intensity of water-suspended solids and is the cause of suspended particles inside the water body influencing turbidity and transparency. A lot of salts are present in water as dissolved form in and the commonly used salts are nitrates of sodium, potassium, calcium, iron and manganese sulphates, carbonates, phosphates, bicarbonates and chlorides [19]. The raw effluent showed 8035 mg/L of TDS and 6.0 mg/L of TSS.

The DO of dye effluent was nil, which may be the heating process involved in the fixation of colour dyestuff with fiber, fabrics and the dye effluent being the higher BOD and COD [20]. also reported the similar findings with zero DO in the dyeing effluent. COD determines the oxygen required for the chemical oxidation of organic matter and non biodegradable matter present in it. COD is also an important pollution indicator that reflects the chemical quality of effluent.

The sample contains 9890 mg/L of COD indicating the presence of heavy pollutants in the effluent. In the analysis of alkalinity and acidity of the dyeing effluent, it was found to be 620 mg/L of alkalinity, and acidity was found to be Below detectable level (BDL) (D.L:1.0 mg/L). The alkalinity of dyeing effluent is dueto dissolved mineral salts, including sulfates, carbonates, and bicarbonates. Chloride is a chief inorganic anions in wastewater. Its presence in textile effluents is mainly attributed to the presence of bleaching agents.

The raw effluent has 2524 mg/L of chloride.Higher chloride contents are harmful to metallic pipes as well as to agricultural crops. The elevatedlevel of salt content in groundwater increases the salinity of soil and causes a severe hazardous effect on the agricultural field [21]. Chloride in textile wastewater isalso high due to the usage of sodium chloride for water softening process [22] Sulphate is an important anion imparting the hardness of the water. Sulfate is not considered toxic to plants or animals at normal concentrations. In humans, smallconcentration causes temporary laxative effects [23]. The sample contains 2290 mg/L. The amounts of TDS, TS, TSS, COD, chloride, and sulfate of effluent were found to be higher than that of CPCB standard. The removal of these pollutants are essential before discharging into the aquatic system.

Table 17.1: Physico-Chemical characterization of dyeing effluent comparison with CPCB standard norms for disposal of effluent

Sr. No	Parameter	Results	UNITS	CPCB Standard(2022) for disposal in surface water
1	pH	8.91	-	6-8.5
2	Color	Green	Hazen Units	400
3	Odor	Unpleasant	-	Odorless
4	Temperature	27	^oC	Shall not exceed 5^oC above the receiving water temperature
5	TS	8041	mg/l	-
6	TDS	8035	mg/l	-
7	TSS	6.0	mg/l	100
8	DO	nil	ml	-
9	COD	9,890	mg/l	250
10	BOD	40	mg/l	30
11	Chloride	2524	mg/l	1000
12	Calcium	10	mg/l	-

Sr. No	Parameter	Results	UNITS	CPCB Standard(2022) for disposal in surface water
13	Phosphate	0.13	mg/l	-
14	Sulphate	2290	mg/l	1000
15	Alkalinity	620	mg/l	-
16	Acidity	BDL (D.L:1.0)	mg/l	-
17	Fluoride	0.68	mg/l	-

17.3.2 Effect of Tamarind Polysaccharide on the Removal of Color, TDS, COD and Chloridefrom Dyeing Effluent:

Polysaccharide in different dosages was used to treat dye effluent for the removal of color, TDS and COD. The treatment revealed a slight change in pH, but still remained alkaline range.

The color removal percentage of various dosages of polysaccharide treatment such as 0.1g, 0.2g, 0.3g, 0.4g, 0.5g and 0.6g were 69%, 71%, 73%, 78% , 82% and 82% respectively. The highest removal of all other parameters were recorded in 0.5g treatment.

About 81% of TDS, 77% of COD and 76% of chloride removal were obtained at 0.5g of dosage treatment. The removal of TDS, COD and Chloride was reduced when increased the polysaccharide dosage concentration beyond the optimum dose i.e. 0.5g.

It is thus suggested that, 0.5g of polysaccharide might be the optimal dosage for the treatment of dye effluent due to attaining the maximum equilibrium state of the coagulation process i.e. agglomeration saturation level.

Natural coagulants are involved in the interparticle bridging, patch aggregation, Charge neutralization and flocculation are responsible to coagulate the pollutants [24], hence the removal was achieved.

Chloride removal mechanism of isolated *Tamarindus indica* seed also reported, the chloride removal mechanism is coagulation due to presence of galactan and galactomannan not adsorption process [25].

Hence, The removal of pollutants from dye effluent was achieved by the coagulation activity of polysachharide such as galactomannan and galactan which are present in the *Tamarindus indica* seed. The polysachharide has cationic nature, which have been bound with pollution causing anionic chemical species of dye effluent, neutralized and formed the flocculation process followed by coagulation process took place, thereby the pollutants from the dye effluent were reduced.

Tamarindus indica seed polysachharide has galactomannan, xyloglucan and galactan are capable of involving coagulation processes. About 92% of TDS and 86% of COD removal were recorded by*Tamarindus indica* seed polysachharide from cheese effluent was also reported [26].

Table 17.2: Effect of Tamarind Polysaccharide on the Removal of Color, TDS, COD And ChlorideRemoval of Dyeing Effluent

Sr. No	Polysaccharide (g)	Color Reduction (%)	TDS Reduction (%)	COD Reduction (%)	Chloride Reduction (%)
1	0.1	69	75	58	63
2	0.2	71	76	72	65
3	0.3	73	78	66	73
4	0.4	78	80	63	75
5	0.5	82	81	77	76
6	0.6	82	81	76	76

17.3.3 Gas chromatography-mass spectroscopy characterization of raw and treated effluent

The GC-MS analysis before treatment of Dye effluent revealed the presence of 30 compounds (figure-3). The identification of the compounds was confirmed based on the peak area (%) and retention time (RT), The first compound identified with less retention time (3.857 and 28.938 min) was 1H-Imidazole, 4,5-dihydro-2-methyl and gamma-Sitosterol respectively. Whereas 5- Aminoimidazole-4-carboxylic acid, methyl ester, and gamma-Sitosterol was the last compound that took the longest retention time (28.938min) to identify. Polysachharide treated dye effluent has shown only 24 compounds (figure-17.4). The reduction of peaks revealed the deprivation of pollutants present in the dye effluent. Similarly bioremediated dye effluent analysis also showed less peaks than raw dye effluent GC-MS analysis [27].

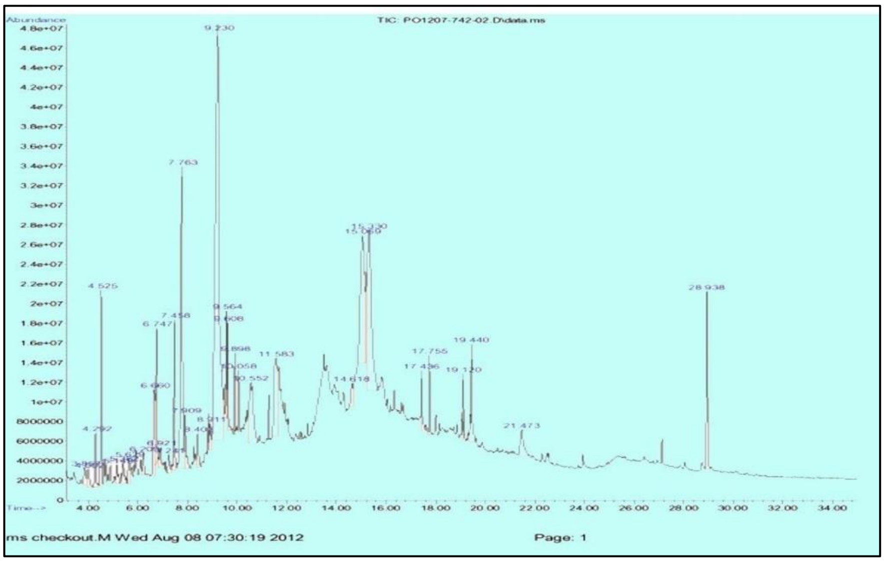

Figure 17.3: Gas Chromatography-Mass Spectroscopy Characterization of raw dye effluent

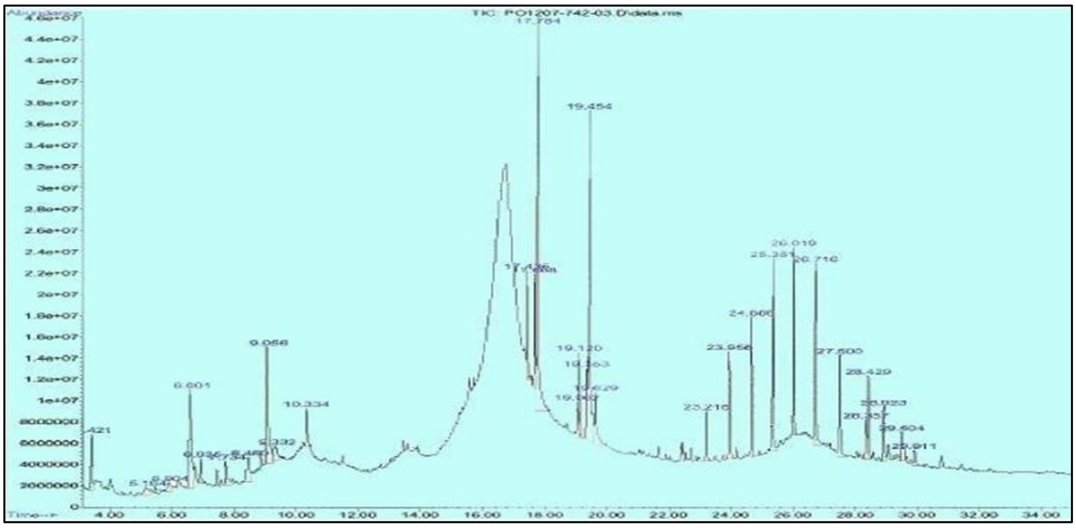

Figure 17.4: Gas chromatography-mass spectroscopy characterization of 0.5g polysahharide treated dye effluent

17.3.4 FTIR analysis of natural coagulant Tamarind. L seed polysaccharide and dye effluent treated sludge:

A spectrum of tamarind L polysaccharide was obtained. The principal absorption peaks of tamarind seed polysaccharide were found at 1366.45 cm-1 (C- O-C, ether group absorbance), 1640.48cm-1 (CO, aldehyde absorption), 2921 cm-1 (C-H stretching), 3343.37 cm-1 (primary OH), which was similar to the results as illustrated by [28-29]. 0.5g of Tamarind. L seed polysaccharide optimum dose sludge was subjected to FTIR analysis to determine the functional groups through peak value. The broad band at 1018.14 cm^{-1} indicated the existence of C-H stretching in polysaccharides. The FTIR spectrum of Tamarind. L have different peaks in different positions. The band at 3275.88 cm^{-1} resembled the presence of the hydrogen- bonded – OH stretching vibration mode ofhydroxyl group, which was similar to the results as illustrated by [30]. The functional group all have involved in the coagulation process followed by removal of colour, TDS and COD causing chemical species from the dye effluent.

Table 17.3: FTIR analysis of natural coagulant Tamarind. L seed polysaccharide

Sr. No	Peak Value cm^{-1}	Functional Group	Interpretation
1	414.28	C=C	Alkene
2	428.27	C=C	Alkene
3	452.74	C=C	Alkene
4	895.09	N-H wag	Primary secondary amines
5	940.70	N-H wag	Primary secondary amines
6	1003.17	C-H “OOP”	Aromatics
7	1366.45	C-O-C	ether

Sr. No	Peak Value cm^{-1}	Functional Group	Interpretation
8	1640.48	CO	Aldehyde
9	2921.69	C-H stretch	Alkane
10	3343.37	O-H stretch	Alcohol

Table 17.4: FTIR analysis of dye effluent 0.5g polysaccharide treated sludge

Sr. No	Peak Value cm^{-1}	Functional Group	Interpretation
1	**Peak Value cm^{-1}**	**Functional Group**	**Interpretation**
2	406.41	C=C	Alkene
3	422.57	C=C	Alkene
4	457.53	C=C	Alkene
5	895.20	N-H wag	Primary secondary amines
6	941.81	N-H wag	Primary and secondary amines
7	1018.14	C-N stretch	Aliphatic amines
8	1403.81	C=C	Aromatic
9	1539.92	N-O asymmetric stretch	Nitro compounds
10	1630.00	N-H bend	Primary amines
11	2920.83	C-H stretch	Alkane

17.4 Conclusion:

In the present investigation concludes that natural coagulants such as Tamarind L seed polysaccharide can be successfully used for the treatment of dye effluent. Polysaccharide was isolated from raw natural coagulants (removal of color, TDS, COD and Chloride). Polysaccharide dosages such as 0.1g, 0.2g, 0.3g, 0.4g, 0.5g and 0.6g have been used for the treatment of dye effluent. 0.5g of polysachharide has been selected as optimum dosage, revealing good treatment potential. The FTIR and GC-MS results also proved the treatment potential of Tamarindus *indica* seed polysachharide.

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