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Physico-Chemical Treatment of Textile Wastewater using Natural Coagulant *Cassia fistula* (Golden Shower) Pod Biomass

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Summary: The use of conventional systems for the treatment of textile industry effluents has made it possible to meet environmental regulations. Due to high cost of the treatment facilities, its implementation is scarce, especially in developing countries, where effluents are discharged into water bodies without any treatment. The internal mass of the Pods of the plant species *C. fistula* (amaltas) contains natural polyelectrolytes which were used as coagulants to clarify turbid textile industry wastewaters. In laboratory tests, direct filtration of turbid wastewater from textile units (dying units: DU and finishing units: FU) with internal mass of the pods of *C. fistula* as coagulant, produced a substantial improvement in the aesthetic and microbiological quality of wastewater from textile units. During the study, following parameters were studied before and after the treatment with *C. fistula* dose: pH, conductivity, hardness , turbidity, salinity, sulfate, total alkalinity as $CaCO_3$, chloride, fluoride, total dissolved solids (TDS), nitrate, nitrite, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), sodium, potassium, calcium and magnesium. Equilibrium data for hardness were fitted using Langmuir and Freundlich isotherm model. The Langmuir model fitted well to sorption data of textile industry (FU) whereas textile industry (DU) sorption data was better described by Freundlich isotherm model. The present method appears suitable for industrial wastewater treatment in heavily industrialized areas of developing and developed countries. This natural coagulant produced 'low risk' wastewater; however, additional disinfection or treatment should be practiced during localized high pollution.

Introduction

Textile wastewater include a large variety of dyes and chemical additions that make the environmental challenge for textile industry not only for liquid waste but also its chemical composition [1]. Main pollution in textile wastewater comes from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Major pollutants in textile wastewaters are suspended solids, oxidizable matter, heat, acidity and other soluble substances [2]. *C. fistula* belongs to family: Fabaceae, genus: *C.*, species: *fistula*. Its common names are amaltas, cana *fistula*, golden shower and Indian laburnum. The fruit (pod) is 30-60 cm long and over 30 cm thick. *C. fistula*'s laxative actions come from a group of well documented compounds called anthraquinones that are found in all *C.* and Senna plants in varying degrees. The seeds contain approximately 2 % anthraquinones, 24 % crude protein, 4.5 % crude fat, 6.5 % crude fiber and 50 % carbohydrates. In addition to the anthraquinone glycosides, other compounds documented in the plant include fistulic acid, rhein, rheinglucoside, galactomannan, sennosides A and B, tannin, phlobaphenes, oxyanthraquinone substances, emodin, chrysophanic acid, fistuacacidin, barbaloin, lupeol, betasitosterol and hexacosanol [3]. The internal pods mass is known to be natural coagulant.

The use of natural materials of plant origin to clarify turbid surface waters was not a new idea. In Sudan, dry *Moringa oleifera* (suhanjana) seeds are used in place of alum by rural women to treat highly turbid Nile water [4]. The extracts of *C. fistula* seeds were found to be mildly active against tested bacteria [5]. The majority of the early work was carried out with a view to establish the viability of using the seeds within household water treatment practices. The present study was carried out to explore the potential of *C. fistula* tropical plant as a new method for its use in the physico-chemical treatment of industrial wastewater. The main objective of the present study was to carry out investigation into the factors and processes involved in the treatment of industrial effluents using dry powder of *C. fistula*

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internal pod mass suspension. Following success in the laboratory we extended our activities to an evaluation of dry powder of *C. fistula* internal pods mass suspension for effectiveness on continuous flow systems used in textile wastewater treatment.

Results and Discussion

Temperature of effluents discharged by textile industry (DU, 43.87 ± 0.02°C) and textile industry (FU, 54.76 ± 0.01°C) were much higher than permissible limit (<35°C). These industries are causing thermal pollution in water bodies. Thermal pollution can lead to decreased dissolved oxygen level in the water while also increasing the biological demand of aquatic organisms for oxygen. In present study, increase in dosage of *C. fistula* from 250 to 1500 mg L^{-1} resulted in improving aesthetic quality of wastewater but further increase in dosage did not produce any significant effect on wastewater quality. The experi-mental results are tabulated in Tables 1-3 and graphi-cally represented in Figs. 1-9. Results revealed that there is a great extent of variation from textile industry (DU) plant to textile industry (FU) plant. For textile industry (DU) the wastewater sample pH was decreased from 8.68 ± 0.01 to a fairly constant value of 7.41 ± 0.03 which was within the recommended standards [6], whilst for wastewater sample from textile industry (FU), increasing dosage of *C. fistula* from 250 to 1500 mg L^{-1} slightly reduced pH from 11.84 ± 0.01 to 11.77 ± 0.02.

Mostly coagulation was found to be dependent on wastewater pH. For that purpose pH was optimized prior to studying the effect of coagulant dose on physico chemical parameters. It was found that optimum pH for better coagulation was 6 for wastewater of both textile units. The textile wastewater was alkaline for pH reduction hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were used. Sulfuric acid was found to be a better choice because bulky flocks were produced with high settling velocity. From Table-1, it is observed that for initial hardness of 164.55 ± 0.08 mg L^{-1} and 25.55 ± 0.07 mg L^{-1} for textile industries, DU and FU respectively, increasing dosage of *C. fistula* from

Table-1: Effect of *C. fistula* dosage on physico-chemical treatment of textile wastewater.

Physico-Chemical Parameters	Dose of *Cassia fistula* (mg/ L)	Textile industry (DU)	% reduction	Textile industry (FU)	% reduc-tion	Physico-Chemical Parameters	Dose of *Cassia fistula* (mg/ L)	Textile industry (DU)	% reduction	Textile industry (FU)	% reduction
pH	0	8.68 ± 0.01	-	11.84 ± 0.01	-	Hardness, As $CaCO_3$ (mg/ L)	0	164.55 ± 0.08	-	25.55 ± 0.07	-
	250	8.30 ± 0.01	-	11.84 ± 0.02	-		250	94.02 ± 0.03	42.85	12.46 ± 0.04	51.21
	500	8.17 ± 0.01	-	11.84 ± 0.01	-		500	58.88 ± 0.05	64.21	6.03 ± 0.05	76.37
	750	8.04 ± 0.03	-	11.83 ± 0.01	-		750	16.29 ± 0.09	90.09	2.02 ± 0.07	92.07
	1000	8.01 ± 0.02	-	11.80 ± 0.03	-		1000	4.86 ± 0.04	97.04	0.42 ± 0.04	98.34
	1250	7.63 ± 0.02	-	11.77 ± 0.01	-		1250	1.65 ± 0.02	98.99	0.16 ± 0.05	99.35
	1500	7.41 ± 0.02	-	11.77 ± 0.02	-		1500	0.99 ± 0.05	99.39	0.11 ± 0.01	99.53
Conductivity (μSCm^{-1})	0	1420.63 ± 0.05	-	3209.57 ± 0.05	-	Total Alkalinity, mg $CaCO_3$/ L	0	64.16 ± 0.03	-	560.48 ± 0.35	-
	250	1418.95 ± 0.03	0.11	2767.41 ± 0.02	13.77		250	48.25 ± 0.01	24.79	512.15 ± 0.23	8.62
	500	1172.53 ± 0.03	17.46	2118.57 ± 0.03	33.99		500	48.43 ± 0.01	24.51	498.18 ± 0.29	11.11
	750	960.32 ± 0.04	32.40	1692.33 ± 0.04	47.27		750	48.84 ± 0.02	23.87	462.26 ± 0.34	17.52
	1000	810.09 ± 0.06	42.97	1285.46 ± 0.05	59.94		1000	48.59 ± 0.03	24.26	452.48 ± 0.52	19.26
	1250	634.94 ± 0.01	55.30	1082.67 ± 0.01	66.26		1250	46.64 ± 0.04	27.30	424.59 ± 0.55	24.24
	1500	317.88 ± 0.01	77.62	363.25 ± 0.01	88.68		1500	44.75 ± 0.06	30.25	394.24 ± 0.34	29.66
Tubidity NTU	0	66 ± 0.13	-	69 ± 0.12	-	Chloride (mg/ L)	0	1020.15 ± 0.96	-	3960.48 ± 1.95	-
	250	53 ± 0.11	19.69	62 ± 0.19	10.14		250	839.15 ± 0.85	17.74	2779.15 ± 2.03	29.82
	500	46 ± 0.14	30.30	56 ± 0.11	18.84		500	625.14 ± 0.89	38.72	1865.23 ± 2.19	52.90
	750	38 ± 0.10	42.42	48 ± 0.17	30.43		750	480.89 ± 0.46	52.86	1489.65 ± 1.65	62.38
	1000	36 ± 0.11	45.45	41 ± 0.19	40.57		1000	340.15 ± 0.73	66.65	1163.48 ± 1.42	70.62
	1250	34 ± 0.11	48.48	35 ± 0.11	49.27		1250	247.59 ± 0.21	75.73	820.95 ± 1.75	79.27
	1500	32 ± 0.10	51.51	27 ± 0.11	60.86		1500	219.78 ± 0.38	78.45	440.75 ± 0.95	88.87
Salinity (ppt)	0	0.59 ± 0.01	-	7.00 ± 0.02	-	TDS (mg/ L)	0	3050.11 ± 1.02	-	5559.23 ± 1.99	-
	250	0.59 ± 0.01	0.00	6.73 ± 0.01	3.85		250	2536.36 ± 1.09	16.84	4745.26 ± 1.84	14.64
	500	0.58 ± 0.01	1.69	6.52 ± 0.01	6.85		500	1347.58 ± 1.10	55.81	4192.13 ± 1.29	24.59
	750	0.57 ± 0.01	3.38	6.23 ± 0.03	11.00		750	1136.25 ± 0.96	62.74	3359.45 ± 1.76	39.56
	1000	0.53 ± 0.01	10.16	5.90 ± 0.01	15.71		1000	1096.25 ± 0.92	64.05	2125.98 ± 1.49	61.75
	1250	0.46 ± 0.01	22.03	5.61 ± 0.02	19.85		1250	723.52 ± 0.95	76.27	1418.92 ± 1.33	74.47
	1500	0.41 ± 0.01	30.50	5.40 ± 0.02	22.85		1500	426.36 ± 0.62	86.02	645.2 ± 1.02	88.39

± "represent Standard deviation"
DU = dying Unit
FU = finishing Unit

250 to 1500 mg L^{-1} results in increasing hardness reduction and almost over 99 % residual hardness removal was achieved from effluents of both industries. The rate of hardness reduction was found to be higher at medium dosage (750 mg L^{-1}) for the effluents of both textile industrial units. At a *C. fistula* dosage of 1500 mg L^{-1}, hardness had reduced almost to zero. It means that at higher *C. fistula* dosage complete removal of residual hardness is possible. In another study at a *Moringa oleifera* dosage of 1800 mg L^{-1}, calcium hardness of synthetic hard water had reduced to zero [7]. At a dosage of 1500 mg L^{-1} the total reduction in conductivity was 77.62 % for textile industry (DU) and 88.68 % for textile industry (FU). This % reduction in conductivity was due to coagulation of mobile ions present in effluent samples. Textile industry (DU) effluent was found to be less saline and further decrease in salinity was observed after application of coagulant. Slightly saline wastewater samples from textile industry (FU) become less saline after the coagulation process. More than 50 % reduction in turbidity was observed for both textile industrial units at a dosage of 1500 mg L^{-1} of *C. fistula*. The reduction in turbidity was due to settling down of suspended solids.

The slight decrease in alkalinity of all wastewater samples from both textile units might be due to precipitation of insoluble products of the reaction between the *C. fistula* and the hardness-causing ions similar to precipitation softening using *Moringa oleifera* and lime/ soda ash. Some of the precipitates (solids/ flocks) were bulky and settled easily on staying while other were light and did not settle easily. The overall reduction in alkalinity was only 30 % for the wastewater sample of both units of textile industry. *C. fistula* is known to be a natural cationic polyelectrolyte and flocculant. As a polyelectrolyte it may therefore be postulated that *C. fistula* removes hardness in water through adsorption and inter-particle bridging [8]. Recommended level of chloride ions for good quality domestic water is 250 mg L^{-1} but effluents of both textile industry (DU) and textile industry (FU) had more chloride ions than recommended level. Effluent of textile industry (FU) has extremely high level of chloride ions. Chloride ions become more toxic when they combine with other toxic substances such as cyanides, phenols and ammonia [9]. Reduction in chloride ions achieved was 78.45 % and 88.87 % at a *C. fistula* dosage of 1500 mg L^{-1} in case of textile industry DU and FU respectively. Data showed that on all dosage the % chloride ion removal is more when the initial chloride ion concentration was above 3900 mg L^{-1}. This may be due to high capability of coagulant for chloride ion removal when the concentration of chloride ion is high. A plot between % TDS removal and dose of *C. fistula* (mg L^{-1}) shown for textile industry (DU) in Fig. 1, revealed a sharp increase in % TDS removal initially at low dosage of 500 mg L^{-1} followed by decreasing rate at intermediate dosage before leveling off at high dosages. While in case of textile industry (FU) (Fig. 1) a somewhat linear relationship between % TDS removal and dosage of *C. fistula* (mg L^{-1}) is observed although at an intermediate dosage and this effect is less pronounced. The total reduction in TDS in case of textile industry (DU) is 86.02 % and 88.39 % for textile industry (FU). The results are consistent with those found in literature. Jones and Brown [4] treated dairy manure (initial total solids of 2.67, 1.89 and 1.32 %) with alum and obtained 93-99 % dissolved reactive phosphorous at dosage of 10 mM Al/ L [reported as optimal rate] using sedimentation periods from 0 to 8 h. Nitrates are present within recommended range in both industrial effluents. It is observed from obtained data that *C. fistula* has more ability for the removal of nitrite as compared to nitrate from wastewater samples of both textile units.

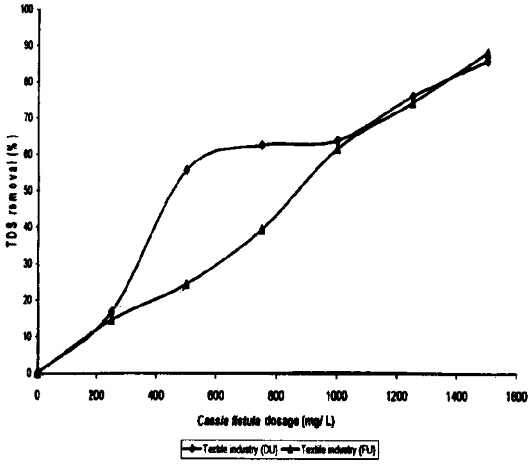

Fig. 1: Effect of *Cassia fistula* dosage on % removal of total dissolved solids (TDS).

There appeared to be little impact of the coagulant treatment on DO of the effluent samples.

Table-2: Effect of *C. fistula* dosage on physico-chemical treatment of textile wastewater.

Physico-Chemical Parameters	Dose of *Cassia fistula* (mg/ L)	Textile industry (DU)	% reduc-tion	Textile industry (FU)	% reduc-tion	Physico-Chemical Parameters	Dose of *Cassia fistula* (mg/ L)	Textile industry (DU)	% reduc-tion	Textile industry (FU)	% reduc-tion
Nitrate (mg/ L)	0	1.09 ± 0.01	-	3.56 ± 0.02	-	DO (mg/ L)	0	7.26 ± 0.02	-	7.48 ± 0.03	-
	250	1.04 ± 0.01	4.58	3.52 ± 0.02	1.12		250	7.32 ± 0.01	-	7.59 ± 0.02	-
	500	1.02 ± 0.02	6.42	3.34 ± 0.01	6.17		500	7.45 ± 0.02	-	7.62 ± 0.03	-
	750	1.02 ± 0.02	6.42	3.45 ± 0.02	3.08		750	7.56 ± 0.01	-	7.84 ± 0.04	-
	1000	1.01 ± 0.01	7.33	3.47 ± 0.03	2.52		1000	7.58 ± 0.01	-	7.78 ± 0.01	-
	1250	1.01 ± 0.01	7.33	3.42 ± 0.01	3.93		1250	7.69 ± 0.03	-	7.80 ± 0.03	-
	1500	1.00 ± 0.01	8.25	3.41 ± 0.01	4.21		1500	7.84 ± 0.01	-	8.09 ± 0.01	-
Nitrite (mg/ L)	0	10.23 ± 0.01	-	14.26 ± 0.05	-	BOD (mg/ L)	0	556.23 ± 0.23	-	1412.23 ± 0.86	-
	250	9.02 ± 0.02	11.82	13.26 ± 0.04	7.01		250	542.25 ± 0.21	2.51	1206.35 ± 0.91	14.57
	500	9.56 ± 0.02	6.54	13.48 ± 0.06	5.46		500	540.15 ± 0.16	2.89	1201.64 ± 0.75	14.91
	750	9.45 ± 0.01	7.62	11.26 ± 0.06	21.03		750	523.01 ± 0.11	5.97	1159.26 ± 0.71	17.91
	1000	8.02 ± 0.02	21.60	10.23 ± 0.01	28.26		1000	514.98 ± .12	7.41	1112.36 ± 0.77	21.23
	1250	8.47 ± 0.01	17.20	9.26 ± 0.07	35.06		1250	516.25 ± 0.32	7.18	1085.94 ± 0.34	23.10
	1500	7.25 ± 0.01	29.13	8.24 ± 0.04	42.21		1500	502.03 ± 0.76	9.74	958.24 ± 0.29	32.14
Sulphate (mg/ L)	0	834.25 ± 0.58	-	943.26 ± 0.69	-	COD (mg/ L)	0	985.45 ± 0.97	-	2865.84 ± 0.94	-
	250	826.54 ± 0.23	0.92	923.65 ± 0.42	2.07		250	887.45 ± 0.95	9.94	2432.58 ± 0.92	15.11
	500	716.25 ± 0.26	14.14	775.26 ± 0.37	17.81		500	856.15 ± 0.82	13.12	2156.48 ± 0.82	24.75
	750	603.21 ± 0.51	27.69	623.19 ± 0.86	33.93		750	858.15 ± 0.49	12.91	1845.28 ± 0.73	35.61
	1000	556.48 ± 0.78	33.29	500.63 ± 0.54	46.92		1000	851.24 ± 0.67	13.61	1849.26 ± 0.64	35.47
	1250	426.15 ± 0.65	48.91	456.92 ± 0.49	51.55		1250	815.26 ± 0.53	17.27	1542.45 ± 0.57	46.17
	1500	298.32 ± 0.36	64.24	284.25 ± 0.37	69.86		1500	616.32 ± 0.43	37.45	819.85 ± 0.69	71.29

± "represent Standard deviation"
DU = dying Unit
FU = finishing Unit

The oxygen level increased relatively after treatment, although they are generally always below the minimum DO concentration for Core Salmon rearing (9.5 mgL^{-1}) both before and after coagulant treatment. The BOD is used as an approximate measure of the amount of biochemically degradable organic matter present in a sample. The permissible limit for BOD is <500 mg L^{-1}. Although % removal of BOD is more in case of textile industry (FU) but after treatment wastewater samples from textile industry (DU) reached permissible limit, it is so because initial BOD of latter is less than of former. The ability of *C. fistula* to decrease BOD represents its capacity to reduce oxygen demanding micro-organisms.

The efficiency of COD removal is dependent on initial COD of sample and is greater at higher dosage of coagulant. For 985.45 ± 0.97 mgL^{-1} initial concentration of COD, 37.45 % reduction in COD value at a dosage of 1500 mgL^{-1} is observed for textile industry (DU), whilst for textile industry (FU) at the same dosage total COD reduction was found to be 71.39 % at initial concentration of 2865.84 ± 0.94 mgL^{-1}. The results reveal more effectiveness of coagulant at COD values approximately nearer to 2800 mgL^{-1}. Chemical Oxygen Demand (COD) is a vital test for assessing the quality of effluents and wastewaters prior to discharge. The COD test predicts the oxygen requirement of the effluent and is used for monitoring and control of discharges and for assessment of treatment plant performance. The impact of an effluent on the receiving water is predicted by its DO. This is because the removal of oxygen from the natural water reduces its ability to sustain aquatic life. The COD test is therefore performed as a routine in laboratories of water utilities and industrial companies.

Sulfate in effluent streams of both industries is above permissible level of 250 mg L^{-1}. In industrial wastewaters containing sulfate ion localized corrosion of iron, steel and aluminum in plants and pipe work can occur through the action of sulfate-reducing bacteria. More than 64 % removal of sulfate ion is achieved at coagulant dosage of 1500 mgL^{-1} although none of the dosage reduced sulfate ions to recommended level.

Fig. 2 illustrates the deviation in Na^+ removal with varying dosage of coagulant for textile dying and finishing units. The results indicate that Na^+ removal efficiency increases as the amount of *C. fistula* increases. This trend is linear in case of textile industry (DU) as compared to textile industry (FU). At a dosage of 1500 mgL^{-1} the Na^+ removal

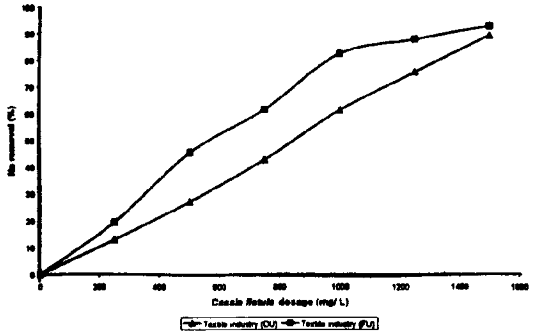

Fig. 2: Effect of *Cassia fistula* dosage on % removal of sodium ion (Na^+).

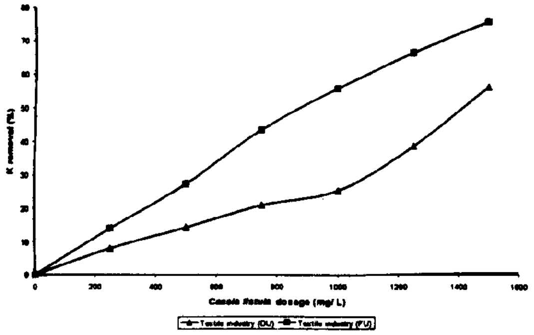

Fig. 3: Effect of *Cassia fistula* dosage on % removal of potassium ion (K^+).

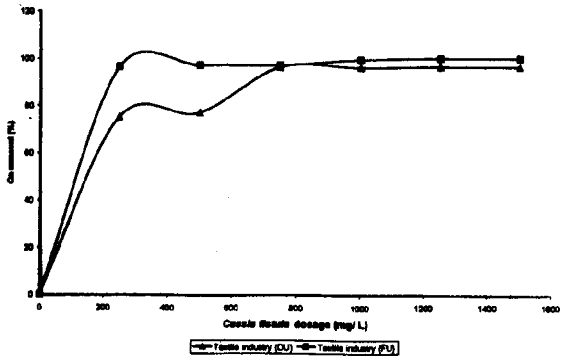

Fig. 4: Effect of *Cassia fistula* dosage on % removal of calcium ion (Ca^{2+}).

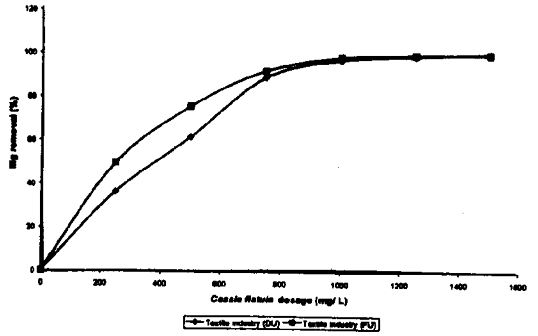

Fig. 5: Effect of *Cassia fistula* dosage on % removal of magnesium ion (Mg^{2+}).

efficiency was 88.91 % and 92.43 % in case of DU and FU of textile industries respectively. Fig. 3 describes the effect of initial coagulant dosage at % K^+ removal. Linear relationship between *C. fistula* dosage and % K^+ removal is observed for textile industry (FU) while in case of textile industry (DU) the trend is linear at lower concentrations, slight decrease in % K^+ removal at medium concentration and increase in % K^+ removal is prominent after dosage of 1000 mgL^{-1} to 1500 mgL^{-1} of natural coagulant *C. fistula*. Fig. 4 and 5 show that the % removal of alkaline earth metals (Ca^{2+} and Mg^{2+} in present case) is increased up to the concentration of 800 mg L^{-1} and then becomes constant after this dosage. The trend is almost similar in wastewater samples from both textile industrial units. Ca^{2+} and Mg^{2+} removal is more than 96 and 99 % respectively. It is observed that for initial concentration of 0.34 ± 0.01 mg L^{-1} increasing dosage of *C. fistula* from 150 to 1250 mg L^{-1} results in increasing % Ca^{2+} reduction and at a dosage of 1250 mg L^{-1} the 100 % Ca^{2+} removal is achieved in case of effluent from textile finishing unit. From experimental results it is also evaluated that the % removal of divalent metal ions is more as compared to monovalent metal cations at all dosage of *C. fistula*.

Adsorption Isotherms

Modeling the equilibrium data is fundamental for the industrial application of coagulation since it gives information for comparison among different materials under different operational conditions, designing and optimizing operating procedures [10] Hardness is the most important parameter to assess aesthetic quality of wastewater, so this parameter is selected for the evaluation of coagulation process by adsorption isotherms. To examine the relationship between sorbed (*q*) and aqueous concentrations (*Ce*) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. The Langmuir and Freundlich adsorption constants evaluated for hardness from the isotherms with correlation coefficients are presented in Table-3. The Langmuir parameters (Figs. 6 and 7) can be determined from a linearized form of equation (1), represented by:

$$1/ qe=1/ q_{max} + 1/ b\ q_{max}\ Ce \qquad (1)$$

Table-3: Langmuir and Freundlich isotherm parameters for % hardness removal from effluents textile industry (DU and FU).

Textile Industry	Langmuir isotherm parameters			Experimental	Freundlich isotherm parameters			
	q_{max} mg g-1	b (L/ mg)	R^2	q (mg/ g)	q (mg/ g)	K (mg/ g)	R^2	1/ n
Dying Unit (DU)	22.123	0.918	0.917	10.903	11.45	11.526	0.950	0.1804
Finishing Unit (FU)	3.926	6.242	0.921	1.695	1.42×10^{-4}	2.842	0.974	0.214

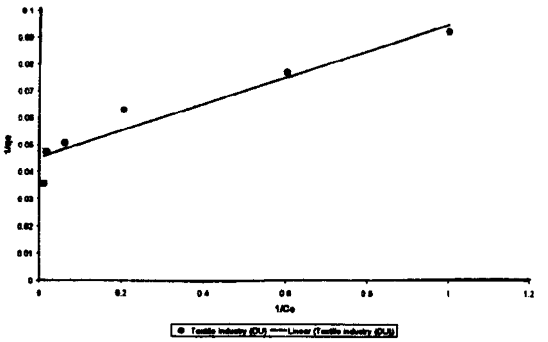

Fig. 6: Langmuir isotherm plot for hardness removal from effluents of textile industry (DU).

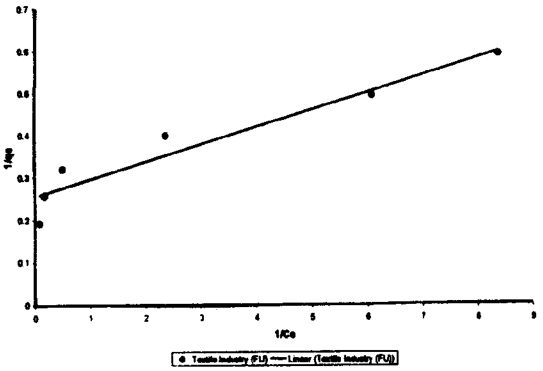

Fig. 7: Langmuir isotherm plot for hardness removal from effluents of textile industry (FU).

Where q_e is metal ion sorbed (mg/ g), *Ce* is the equilibrium concentration of metal ion solution, mgL^{-1}, q_{max} and b are the Langmuir constants. Adsorption-partition constants are determined for hardness using the following log form of the Freundlich isotherm equation (2), represented by:

$$\log q_e = 1/ n \log Ce + \log K \qquad (2)$$

Where q_e is metal ion sorbed (mg/ g), *Ce* is the equilibrium concentration of metal ion solution, mgL^{-1}, K and 1/ n are constants. The constants K and 1/ n are determined by linear regression from the plot of log q against log *Ce* (Figs. 8 and 9). K is a measure of the degree or strength of adsorption, while 1/ n is used as an indication of whether adsorption remains constant (at 1/ n = 1) or decreases with increasing adsorbate concentrations (with $1/ n \neq 1$). The q_{max} value is the maximum value of q_{eq}, which is important to identify which biosorbent shows the highest uptake capacity and as such is useful in scale-up considerations. The maximum capacity q_{max} defines the total capacity of coagulant for removal of hardness. In case of textile industry (DU) the equilibrium data are well described by Freundlich adsorption isotherms as represented by high value of correlation coefficient. Fitting of Freundlich model to DU data revealed that adsorption was heterogeneous. While in case of textile industry (FU) reduction in hardness by coagulant followed well Langmuir isotherm and represents that monolayer of sorbate is formed on sorbent. The higher values of hardness for the textile industry (DU) samples as compared to textile industry (FU) are due to the fact that more hardness causing species are used in dying operations. It contains hardness due to calcium, magnesium and other hardness-causing substances. This implies that as the number of hardness-causing species increases, the required dosage of *C. fistula* increases.

It is also observed that the some solids (flocks) after rapid mix become bulky and settled down rapidly while others are rod like and light. They therefore settled down slowly. In practice there may be the need for the provision of a filtration system by sedimentation followed by the filtration for continuous flow wastewater treatment systems. Results of these preliminary studies have shown that *C. fistula* seeds have considerable potential to be used

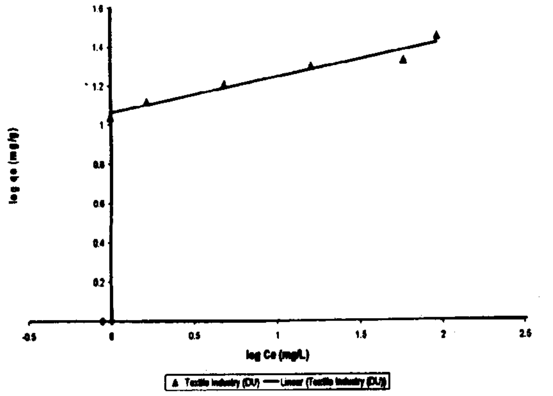

Fig. 8: Freundlich isotherm plot for hardness removal from effluents of textile industry (DU).

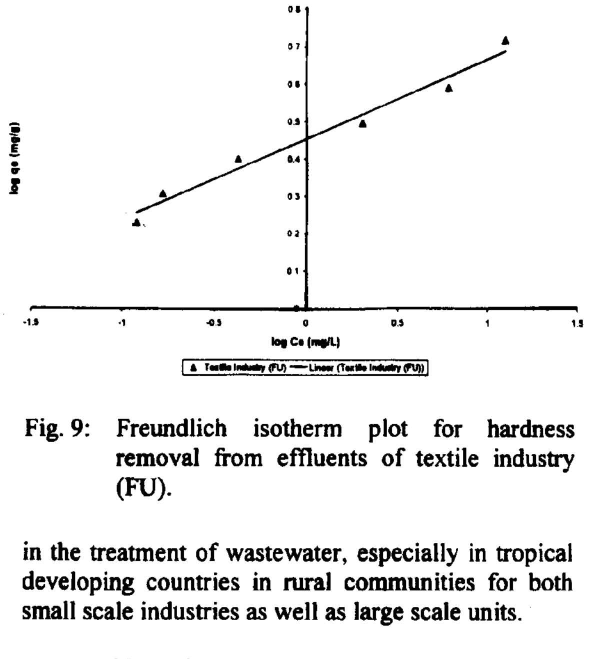

Fig. 9: Freundlich isotherm plot for hardness removal from effluents of textile industry (FU).

in the treatment of wastewater, especially in tropical developing countries in rural communities for both small scale industries as well as large scale units.

Natural coagulant used in the present study should not cause serious health hazard because *C. fistula* possesses medicinal properties useful in the treatment of skin diseases, inflammatory diseases, rheumatism, anorexia and jaundice [11]. A bioactive flavone glycoside 5,3',4'-tri-hydroxy-6-methoxy-7-*O*-*alpha*-*L*-rhamnopyranosyl-(1-->2)-*O*-*beta*-D-galactopyranoside with antimicrobial activity is reported [12]. Four compounds, 5-(2-hydroxyphenoxymethyl) furfural,(2'*S*)-7-hydroxy-5-hydroxymethyl-2-(2'-hydroxylpropyl) chromone, benzyl 2-hydroxy-3,6-dimethoxybenzoate and benzyl 2.beta-*O*-*D*-glucopyranosyl-3,6-dimethoxybenzoate, together with four known compounds, 5-hydroxymethylfurfural, (2'S)-7-hydroxy-2-(2'-hydroxypropyl)-5-methylchromone and two oxyanthraquinones, chrysophanol and chrysophanein, are also isolated from the seeds of *C. fistula* by Kuo *et al.,* [13]. Trolox equivalent antioxidant capacity and ferric-reducing antioxidant power assays show that the antioxidant activities are strongly correlated with total phenols [14]. The heaptoprotective activity [15-16] and the hypoglycaemic activity [17] have been reported. Excellent antimicrobial properties suggest that *C. fistula* internal pod mass as water purifiers should not constitute a serious health hazard. Economic figures are presently not available and there is a need for studies at pilot scale in order to compare costs, *i.e.* pods, pods preparation, storage, *etc.* Finally, it is recommended that efforts be made to carry out further studies at pilot plant level to provide the necessary data for field applications.

Experimental

Wastewater samples from textile industries (DU and FU), were used for the laboratory based experimental runs.

Sample Collection

The sites for sample collection were within the city zone of Faisalabad-Pakistan. Each site was visited once a week and triplicate samples were collected from various parts of the system from all industries during one year period from August, 2004 to August, 2005. Samples were collected in polyethylene bottles [18] and placed in a cooler for transportation. Once all the samples were collected, they were brought back to the analytical laboratory, located in Department of Chemistry, University of Agriculture, Faisalabad-Pakistan, where physico-chemical parameters were analyzed in industrial effluent samples. All instruments used in study were properly calibrated before analysis according to user's manual.

Preparation of C. fistula Internal Pod Mass Suspension

Dry *C. fistula* pods were collected from main campus, University of Agriculture, Faisalabad, Pakistan. Wings and coat from selected good quality *C. fistula* pods were removed and the internal mass ground to a fine powder using food processor (Moulinex, France) and then sieved through Octagon siever (OCT-DIGITAL 4527-01). This was done to remove any large size particles and to obtain coagulant with a known particle size. The fraction with ≥0.255mm was selected for use in the laboratory tests. The sieved material was stored in an air tight plastic container for further experiments. Two grams of the powder and 200 ml distilled water were put in a high speed mixer (ATO MIX MSE) and blended for 30 s to extract the active ingredients. The resulting suspension was filtered through a muslin cloth and the filtrate volume was made up to 500 ml to give a stock solution of approx. 4000 mg/ l. The solution had a pH of 6. The stock solution was prepared fresh for use as and when needed, since its deterioration sets in if stored for more than two days at room temperature.

Experimental Runs

For each experimental run 500 ml of industrial wastewater sample was put in a one litre beaker and the paddle of a jar apparatus (Voss Flocculator) inserted. Coagulation was stirred for 5 min at 100 rpm for flash mixing (required dosage was added and stirred) and the wastewater sample followed by 30 min of slow agitation at 30 rpm using a portable electronic tachometer (Banair).

For industrial effluent samples, water quality parameters were measured before and after dosing. Since some of the flocks formed after each experimental run were light and therefore did not settle as fast as required during the one hour settling period, the product water was filtered before carrying out the measurement of the water quality parameters. After one hour settling pH (4500-H^+B) and salinity (2520B) and Conductivity (2510B) were determined using Innolab pH and Conductivity meter. Hardness was determined from separate determination of Ca^{2+} and Mg^{2+} (2340B). Dissolved oxygen (DO) and biological dissolved oxygen (BOD) were determined by Dissolved Oxygen Meter model Acorn DO6 using standard methods 4500-0G and 5210B respectively. Turbidity was estimated by nephelometeric method using LaMotte 2020 Portable Turbidity Meter (2130B), total alkalinity as $CaCO_3$ was estimated by titration standard methods 2320B, total dissolved solids (TDS) were determined by standard method 2540C [19]. Chemical oxygen demand (COD) was determined using closed reflux method [20]. Chloride, nitrate, nitrite and sulfate were determined by titration methods approved by UNEP/ WHO [21]. Sodium and potassium were estimated by flame photometer (The Sherwood Model 41O). Calcium and magnesium ions were determined using atomic absorption spectrophotometer (AAnalyst 300, Perkin Elmer) [22].

Conclusions

1. When toxic substances from industrial effluents enter into lakes, streams, rivers, oceans and other water bodies, they get dissolved or lie suspended in water or get deposited on the bed. This results in the pollution of water whereby the quality of the water deteriorates, affecting aquatic ecosystems. Pollutants can also seep down and affect the groundwater deposits.
2. The effects of water pollution are not only devastating for people but also for animals, fish and birds.
3. The treatment of any form of waste before disposal into the environment is important and ensures safety of the populace. Use of material of natural origin makes the waste treatment more economical and valuable in developing countries.
4. The efficiency of treating physico-chemical parameters of textile industry (DU and FU) using *C. fistula* (internal pod mass) was found to be dependent on dosage of coagulant as well as pH of wastewater.
5. Optimized dosage for highest % reduction in physico-chemical parameters of textile industry (DU and FU) using *C. fistula* (internal pods mass) was found to be 1500 mg L^{-1}
6. *C. fistula* has potential to be used in the physico-chemical treatment of effluents from textile industries.

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References

1. M. C. Venceslau, S. Tom and J. J. Simon, *Env. Technol.*, **15**, 917 (1994).
2. A. Dae-Hee, C. Won-Seok and Y. Tai-Il, *Process Biochem.*, **34**, 429 (1999).
3. J. P. Roskoski, G. C. Gonzalez, M. I. F. Dias, E. P. Tejeda and Y. A. Vargas-Mena, Woody Tropical Legumes: Potential Sources of Forage, Firewood and Soil Enrichment, 135 (1980).
4. R. M. Jones and S. P. Brown, Chemical and Settling Treatment of Dairy Wastewater for Solids Separartion and Phosphorous Removal. In proc. 8th International Symposium for Animal, Agriculure and Food Processing Wastes, De Moines, IA: ASAE, 132 (2000).
5. M. A. Ali, M. A. Sayeed, M. S. A. Bhuiyan, F. I. Sohel and M. S. Yeasmin, *J. Med. Sci.*, **4**, 24 (2004).
6. U. S. Environmental Protection Agency (EPA), Drinking Water Regulations and Health Advisories, EPA 822-R-94-001, (1994).
7. S. A. Muyibi and L. M. Evison, *Water Res.*, **29**, 1099 (1995).
8. V. K. LaMer and T. W. Healy, *Rev. Appl. Chem.*, **13**, 112 (1963).
9. Quality Criteria for Water, U. S. Environmental Protection Agency, (1976).
10. B. Benguella and H. Benaissa, *Water Res.*, **36**, 2463 (2002).
11. K. R. Kirtikar and B. A. Basu, Indian Medicinal plants. 2nd edi, Periodical Experts Book Agency, New Delhi, **2**, 856 (1991).
12. R. N. Yadava and V. Verma, *J. Asian Nat. Prod Res,*. **5**, 57 (2003).
13. Y. H. Kuo, P. H. Lee and Y. S. Wein, *J. Nat. Prod,*. **65**, 1165 (2002).
14. A. Luximon-Ramma, T. Bahorun, M. A. Soobrattee and O. I. Aruoma, *J. Agric. Food Chem.*, **50**, 5042 (2002).
15. T. Bhakta, P. K. Mukherjee, K. Mukherjee, S. Banerjee, S. C. Mandal, T. K. Maity, M. Pal and B. P. Saha, *J. Ethnopharmacol. Sep.*, **66**, 277 (1999).
16. T. Bhakta, S. Banerjee, S. C. Mandal, T. K. Maity, B. P. Saha and M. Pal, *Phytomedicine*, **8**, 220 (2001).
17. M. E. Avella, A. Diaz, I. De Gracia, R. De Tello and M. P. Gupta, *Rev. Med. Panama.*, **16**, 39 (1991).
18. Environment Canada, Analytical Methods Manual. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. (1981).
19. A. E. Greenberg, L. S. Clesceri and A. D. Eaton, *Standard Methods for Examination of Water and Wastewater,* 18th Edition, Ch 2, 1(1992).
20. S. A. Abbasi, *Chemical Oxygen Demand: Water Quality Sampling and Analysis*. Discovery Publishing House, New Dehli, 141 (1998).
21. R. Balance, Physical and Chemical Analyses. Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes, UNEP/ WHO, Ch 7, 1 (1996).
22. H. Hussein, S.F. Ibrahim, K. Kandeel and H. Moawad, H. *E.J. Biotechnol.*, 7, 717 (2004).