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Reduction in Organic Waste through Recovery from Waste Paper Recycling Mill

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Abstract

Paper manufacturing industry is characterized by large amount of water consumption and hence high rate of wastewater generation which is concern to water pollution. This study considers the characterization of paper mill effluents for recovery in the form of Total Suspended Solids (TSS) in relation to decrease in organic waste in the form of Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD). For this purpose sedimentation and coagulation were applied. Coagulation was performed using "Alum" to check its efficiency. The effects of dose rate and settling time of solids were observed for TSS, BOD_5 and COD removal. The average concentrations of TDS (860-881 mg/L), TSS (822-836 mg/L), BOD (261-275 mg/L) and COD (519-550 mg/L) were determined above the permissible limits. By comparing the level of these parameters after sedimentation a visible decrease was observed. TDS, TSS, COD and BOD_5 decrease by 19%, 37%, 17.3% and 18%, respectively. In coagulation treatment the decrease was 84%, 89%, 86% respectively for TSS, COD and BOD_5. The study observed maximum recovery in the form TSS (84%) along with BOD_5 and COD. Therefore, coagulation treatment for paper recycling mill is recommended.

Keywords: Coagulation, sedimentation, coagulant, removal efficiency, BOD_5, COD

Introduction

Paper manufacturing is a water-intensive chemical process are resulting a large amount of wastewater [1]. Demand of paper manufacturing is increasing each year and is more than 300 million tons of wood fiber products. Paper manufacturing is carried out by several techniques such as mechanical, chemical and thermal methods [2]. In these methods the mostly adopted type is mechanical pulping involve grinding of desecrated wooden chips [3]. During paper manufacturing, large quantity of water is required for bleaching and pulping process [4]. As a result same quantity of waste-water is generated and its discharge is a serious problem. These industries are considered as contributors of pollutants to environment in the form of waste-water [5]. The wastewater consists of organic and inorganic matter, COD, BOD_5, TSS and strong colour along with 300 chlorinated compounds [1-6]. Due to high pollutants content the release of untreated wastewater into receiving water bodies is a major environmental concern [7]. In Pakistan, the annual rate of paper manufacturing is 400,000 tons which generate wastewater @ 36,000 m^3/day [8]. This waste-water is not monitored properly and is discharged into nearby water channels which pose harmful threats to aquatic ecosystem. To reduce the rate of wastewater generation, paper manufacturing industries are strictly forced to adopt zero liquid effluent approaches [9]. Wastewater is generally recycled by paper mill to conserve energy and raw materials while its treatment has been considered important to prevent pollution of aquatic ecosystem [10]. Wastewater from paper recycling mill is biodegradable and can be treated easily [7]. The conventional treatment methods applied for wastewater are physical, chemical and biological [11]. Physical treatment includes sedimentation, adsorption, flotation, using physical barriers such as deep bed filters and membranes [12]. Chemical treatment includes coagulation method and has been considered as an important approach for paper mill effluents [13]. Coagulation is a fast treatment method of wastewater in short period of time. It includes salts of strong acids and weak basis such as Alum, ferric chloride, ferrous sulphate etc. as effective coagulants [14]. The advantage of coagulation treatment is the reduction of wastewater pollutants up to lowest level making it cost effective for secondary treatment [15]. While biological treatment is important to remove organic pollutants in wastewater such as trickling filter [12]. Biological treatment is also effective for COD and BOD_5 removal but not efficient in removal of colour and involved high energy consumption [3].

This study is an attempt to analyze paper mill wastewater for recycling and to recover the cellulose content. There are two paper mills working in Hayatabad industrial estate. The paper mills are located with 33°58 ′51.3″ N, 71°25′ 47.6″ E and 33°59′ 46.4″ N, 71°25′ 21.3″ E latitude and longitude respectively. These industries are equipped with machinery to prepare paper from both sources such as wood and paper-waste respectively. In case of non-availability or shortage of raw-wood, the industries recycle paper waste to prepare paper [11]. The paper mills generate large quantities of wastewater which contains higher levels of cellulose content [8]. This wastewater is discharged into industrial drain without any treatment and then finally it joins river Kabul. Such type of untreated wastewater is a threat to aquatic organisms [16]. Therefore, to keep recovering raw materials and keep paper mill environment friendly, arrangements for effluents treatment is considered important for each industry.

Material and Method

No study has been carried out to check the present status of paper mills at Hayatabad Industrial Estate for paper and water recycling. The wastewater discharged from paper mills is rich in cellulose contents and it is an important raw-material used in mold industry for preparation of packing material. To know about the recovery of cellulose and wastewater treatment, paper mills were evaluated. For this purpose, paper mills were visited for processing and interviews were arranged with managers to ask questions about raw material, water consumption, wastewater generation and treatment for recovery of cellulose contents.

Water consumption

To know about water consumption, the paper mill technical staff members and tube well operators were interviewed.

Sample collection

Total 8 composite wastewater samples were collected from paper mills. Each composite sample consists of five grab samples collected at one hour interval. The paper mills are discussed here with the names, Paper mill-A and paper mill-B. Samples were taken in 2-L clean and dried plastic bottles and then brought to laboratory for analysis.

Chemical analysis

The collected waste-water samples were analyzed for physicochemical parameters (pH, EC, TDS, TSS, COD and BOD_5) according to standard methods for the examination of water and waste-water [17]. The pH and electrical conductivity (EC) were measured using pH meter and conductivity meter respectively. Both the pH meter and conductivity meter were calibrated with required buffer solutions to give readings for samples in quickest possible time.

Total Suspended Solids (TSS) and Total Dissolved solids (TDS) were determined by centrifugation method. For suspended solids, 25 ml of wastewater was filtered through a pre-weighted filter paper. The non-filterable material was left on filter paper. This filter paper was then kept in oven at 50°C for some time till it become dry. After drying, it was cooled in desiccators and weighted it again. The difference in initial and final weights of filter paper gave the suspended solids.

The total dissolved solids in wastewater samples were determined by taking 25 ml of sample in a clean pre-weighted china dish. This china dish was kept in oven at 105^{o}C for 24 hours. When the sample was completely evaporated the china dish was removed from oven and cooled it in dissector. Then weighted it again. The difference in weight of china dish before and after sample gave the total dissolved solids.

COD was measured by using open reflux method. In this method, water samples were digested with 0.25 standard solution of potassium dichromate in the presence of sulfuric acid. Mercuric sulfate and silver sulfate were used as catalyst. Then sample was titrated with 0.25 N ferrous ammonium sulfate solution (FAS), using ferroin as indicator. The COD level was determined using equation.

Calculations

$$\textbf{COD (mg/L)} = \frac{(B-T)\ N \times 1000 \times 8}{\text{Volume of Sample used}}$$

Where

T = volume of titrant (FAS) used against sample (ml).
B = Volume of titrant (FAS) used against blank (ml).
N = Normality of titrant (FAS) 0.25N.
Equivalent weight of oxygen is 8.

For BOD_5, 10 ml of wastewater sample was taken in 300 ml of BOD_5 bottle and diluted it till 300 ml with distilled water (2 bottles for each sample). Added 1 ml $MnSO_4$, 1 ml KI and allow it to stand for some time to react with oxygen. When the floc settled down, shacked the contents in bottle by turning it upside and down. Added 1 ml of Conc.H_2SO_4 just above the surface of bottle and then inverted it carefully to dissolve the floc and added 1 ml of starch indicator. The content of one bottle is transferred into flask and subjected to titration against $Na_2S_3So_4$ solution. The reading of burette of day-1 was noted as initial BOD_5. Bottle-2 was kept inside the incubator at 20^{o}C for time period of 5 days. After 5 days, the content of bottle-2 was titrated against $Na_2S_3So_4$ solution until the blue colour disappeared and took the day-5 reading as final reading. The BOD_5 was computed from the difference of day-1 and day-5 readings using the formula.

Calculations

$$BOD_5\ (mg/L) = \frac{D_1 - D_2}{P}$$

D_1= day-1 reading
D_2= day -5 reading
P = volume of sample used

After analysis, results were compared with standards fixed for industrial discharges [18].

Treatment methods

For 100% utilization, the paper mill wastewater was treated in the laboratory. The effluent was subjected to two stage treatment, i) sedimentation and ii) coagulation as discussed below:

Physical treatment (Sedimentation)

First, sedimentation treatment was carried out. In this treatment, 1 liter of each wastewater sample was taken in a graduated cylinder and allowed to stand for 24 hrs without adding any chemical. When the settable particles settled down then each sample was analyzed to find its characteristics.

Chemical treatment (Coagulation)

Coagulation method was applied for TSS removal. In coagulation, Alum ($Al_2\ (SO_4)_3.18H_2O$) was used as a coagulant. Alum is one of the raw materials used by paper mill therefore its selection was preferred for treatment of wastewater. For this purpose, 1000 mg/L stock solution was prepared. One mL of this solution when added to 1 liter sample, was equivalent to 1 mg/L concentration of the coagulant. The sample was subjected to Jar-Test by adding different doses of Alum in combination with alkalinity with a ratio of 2:1 respectively. The Jar apparatus was consisted of three cylinders with capacity of 1 liter each. Samples were shacked well for a minute and then transferred into Jar-Test apparatus. The effect of adding 5 to 50 mg/L of coagulant (Alum) was tested. Settling time and coagulant dosage was investigated for removal efficiency of suspended solids**.** The efficiency of TSS removal was determined in percentage.

As Alum is acidic in nature and affects the coagulation process negatively. Therefore pH was kept above 7 with the help of Na_2CO_3 @ of 0.5 mg/L for each 1 mg/L of Alum [21]. In coagulation treatment, pH was monitored properly for better performance [3].

Percentage reduction of pollutants

The percent removal of pollutants, TSS, TDS, BOD_5, and COD was determined using equation.

$$\text{Percentage Reduction} = \frac{C_1 - C_2 \times 100}{C_1}$$

C_1 refers initial value of pollutant and C_2 refers final value of pollutant [22].

Results and Discussions

The paper mills use ground water with daily consumption of 2176 m^3 and 2614 m^3 to prepare 12-15 tons paper/day. The mills use 72000L water per ton. The daily wastewater discharge was 1936.4 and 2489.5 m^3 by paper mill-A and B respectively. A fraction of this wastewater is recycled in processing but at the end, the water is not recycled and is directly discharged into outside nullah/drain. Studies conducted in 2010 revealed that this wastewater is a continuous source of threat for receiving water body, the Kabul River. It also contaminates the drinking water quality of the nearby areas [11-16].

Analytical results of untreated wastewater

Among water parameters, EC is not defined by Pak-NEQS and was measured as an indicator for treatment. The pH of paper mill effluents ranged between 8.2 and 8.3. The average values of electrical conductivity were 1638 and 1764 uS/cm. Higher value of EC in paper mill effluents is due to the presence of dissolved salts [23]. TDS was observed within the permissible limit in effluents of both paper mills (860-881 mg/L). However, high concentration of TDS increases the chances of turbidity and reduces the solubility of gases such as oxygen [23]. TSS, BOD_5 and COD were found above the permissible limits (Table-1). Literature revealed that discharged effluents of paper mill contain different chemicals. Therefore, paper mill is associated with pollution problems including high TDS, TSS, BOD_5, COD etc. [24].

Paper mill Waste-water after sedimentation treatment

As a result of primary sedimentation, pH was observed with average range of 7.1 and 7.3 in both the paper mills. The average values of EC were 1426 µS/cm to 1483 µS/cm. The application of sedimentation treatment, TDS was reduced up to 15% to 19%. TSS contents were measured in the average range of 537 mg/L to 554 mg/L. About 34-37% suspended solids were removed under sedimentation (Table-2). Thompson et al, (2001) reported that sedimentation is an important and effective pre-treatment for removal of TSS from paper mill effluents [25]. Primary sedimentation has removed BOD_5 to some extent. BOD_5 was reduced from 12% to 18% for paper mill A and B respectively. Final results were above the limit defined in Pak-NEQS [18]. Impact of primary sedimentation was also observed for removal of COD. The level of COD was reduced to 12% and 18% for both paper mills (Table-2).

Paper mill wastewater after coagulation

As mentioned earlier, pH was adjusted above 7.5 by adding alkalinity and was kept within the permissible limits defined in Pak-NEQS [18]. Electrical conductivity was determined with average range of 1511-1562 µS/cm. In coagulation process, EC values increased due to addition of Alum and alkalinity.

The concentrations of TDS were observed increased in treated samples. The increase was due to addition of coagulants and alkalinity. The average contents of removable suspended solids after coagulation ranged between 135 and 141 mg/L. The removal rate of suspended solids was calculated 83 and 84% respectively. The level of BOD_5 was reduced to 36 and 38.5 mg/L with the average percent efficiency of 86% (Table-3). A decreasing trend in settling time was observed with increase in dosage of coagulant. It is due to the decline of colloidal particles by neutralizing the forces that keep colloidal near to each other. Literature revealed that in coagulation process, small particles got combine to form macro molecules in the form of floc which settles down due increase in weight [3].

The content of COD in collected wastewater samples was reduced to 57 and 77 mg/L (86-89%) [26]. Dilek and Gokcay (1994) reported that Alum is one of the best coagulants for COD removal. While Stephenson and Duff (1996) recommended Alum as one of effective coagulant for wastewater treatment [27]. Under coagulation treatment, the maximum removal of BOD_5 was calculated as 86% and COD was 89% respectively (Table-3). Pokhrel and Viraraghavan (2004) suggested coagulation method for treatment of paper mill effluents and strongly encouraged it for removal of BOD_5 [2].

Table- 1 **Results of Untreated Paper Mill Wastewater**

Parameter	Paper Mill-A				Paper Mill-B				Pak-NEQS
	Min	***Max***	***Avg***	***S.D***	***Min***	***Max***	***Avg***	***S.D***	
pH	7.8	8.5	8.2	0.44	7.9	8.6	8.3	0.44	06-10
EC µS/Cm	1689	1754	1738	11.21	1725	1824	1764	11.5	--
TDS mg/L	846	878	860	8.26	862	915	881	7.33	3500
TSS mg/L	814	867	836	7.41	805	844	822	7.2	150
COD mg/L	540	620	550	4.68	511	609	519	4.23	150
BOD_5 mg/L	267	306	275	2.61	270	297	261	2.4	80

Table-2. **Characteristics of Paper Mill Effluents after Sedimentation**

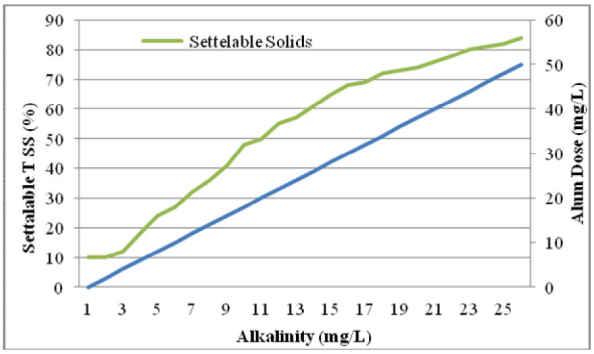
Parameter		Paper Mill-A					Paper Mill-B				
		Min	***Max***	***Avg***	***S.D***	**Removal (%)**	***Min***	***Max***	***Avg***	***S.D***	**Removal (%)**
pH	Before	7.8	8.5	8.2	0.44	--	7.9	8.6	8.3	0.44	--
	After	7.2	7.5	7.3	0.13		7.0	7.4	7.2	0.12	
EC µS/Cm	Before	1689	1754	1738	11.21	--	1725	1824	1764	11.5	--
	After	1447	1486	1483	10.2		1411	1449	1418	10.04	
TDS mg/L	Before	846	878	860	8.26	15	862	915	881	7.33	19
	After	722	740	735	6.2		707	722	706	5.5	
TSS mg/L	Before	814	867	836	7.41	34	805	844	822	7.2	37
	After	477	634	554	8.02		447	659	537	6.14	
COD mg/L	Before	540	620	550	4.68	11.3	511	609	519	4.23	17.3
	After	400	586	488	4.11		364	524	435	3.8	
BOD_5 mg/L	Before	267	306	275	2.61	12	270	297	261	2.4	18
	After	200	292.5	243	3.05		177	282	213	2.76	

Table-3. **Characteristics of Paper Mill Effluents after Coagulation**

Parameter		Paper Mill-A					Paper Mill-B				
		Min	***Max***	***Avg***	***S.D***	**Removal (%)**	***Min***	***Max***	***Avg***	***S.D***	**Removal (%)**
pH	Before	7.8	8.5	8.2	0.44	--	7.9	8.6	8.3	0.44	--
	After	8.1	8.6	8.3	0.31		8.1	8.4	8.2	0.26	
EC uS/Cm	Before	1689	1754	1738	11.21	--	1725	1824	1764	11.5	--
	After	1741	1778	1762	8.22		1702	1722	1711	9.13	
TDS mg/L	Before	846	878	860	4.26	--	862	915	881	4.33	--
	After	868	885	879	4.21		847	860	854	4.03	
TSS mg/L	Before	814	867	836	7.41	84	805	844	822	7.2	83
	After	120	148	135	2.52		126	157	141	2.13	
COD mg/L	Before	540	620	550	4.68	86	511	609	519	4.23	89
	After	34	133	77	1.1		36	98	57	1.2	
BOD_5 mg/L	Before	267	306	275	2.61	86	270	297	261	2.4	86
	After	17	67	38.5	1.2		20	49	36	1.03	

Removal of suspended solids with coagulation

In coagulation process, the minimum removal of suspended solids was observed 20% for a combination of 5:3 of Alum and alkalinity. The addition of 30 mg/L Alum and 25 mg/L of alkalinity, decrease in suspended solids was observed by 68%. The removal efficiency was further increased to 76% by adding 40 mg/L Alum and 20 mg/L of alkalinity. Maximum TSS removal (84%) was possible with 50 mg/L Alum and 25 mg/L of alkalinity (Fig.1). In comparison to sedimentation process, coagulation showed more effectual results in pollution reduction. Therefore coagulation can be considered as a good treatment for recovery of cellulose contents. Literature revealed that increase dosage of coagulant case the decrease in confederations of suspended solids and hence effects to increase its percent removal [28-29].



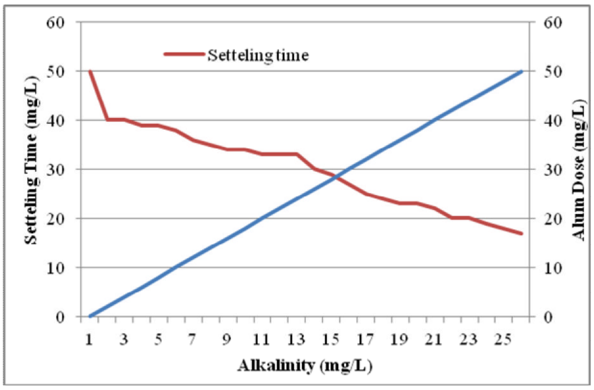


Figure 1. **Effect of Coagulation on Settleable Solids**

Settling time

During coagulation process, visible decrease was observed in settling time along with the removal of suspended solids. The settling time during sedimentation was 24 hours. During coagulation, the combination of 30, 40 and 50 ml of Alum with 15, 20 and 25 ml of alkalinity, the time observed for these combinations was 27, 22 and 17 minutes respectively (Fig.1). The settling time was dependent upon coagulant and alum doses.

Conclusion

The recovery of TSS from paper mill based on waste-paper is possible through simple sedimentation and coagulation. This will not only economize the waste paper recycling process, but will reduced pollution load in term of TSS, BOD_5 and COD. To keep the mill environment friendly, treatment of wastewater by coagulation treatment is suggested.

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