Wastewater Management in Pulp & Paper Industry-Case Study

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A large paper mill in central India produces a range of paper products employing kraft sulphate process using bamboo or hardwood or both in suitable proportions as raw material. Huge quantity of water is used in paper manufacturing, resulting in generation of huge quantity of wastewater. The wastewater generation was in the range of 160 to 195 m^3/t paper produced. Total quantity of wastewater generated at the mill under study was treated at two effluent treatment plants separately. The paper describes evaluation of existing effluent treatment plants, bench scale treatability and pilot plant studies for improvement in quality of treated effluent so as to comply effluent discharge standards prescribed by the regulatory agencies.

Keywords: Paper mill, wastewater, lignin, physico-chemical treatment, chemical dosing, biological oxidation

INTRODUCTION

Paper industry has been one of the most important segments in Indian economy over a past few decades. In the year 1994-95 only 380 paper and paperboard Industries with an installed capacity of 3.84 Million Tones Per Annum (MTPA) were operational in the country, however, due to certain technical problems; actual production was only 2.57 MTPA (1). Subsequently, in the recent years, the numbers of industries are increased to 480 and today, about 515 pulp & paper industries with an installed capacity of 5.108 MTPA were reported (2). Based on annual growth rate of 6.5 % over the period of six years (2000-2006), the paper demand in 2005-06 is expected to be 5.48 MTPA (3). In India, paper mills vary in sizes depending on raw materials, manufacturing process, products and adopted waste management systems (4). Originally, Indian paper industries utilized only bamboo as the main raw material for production of cellulose. However, in recent years due to short supply of bamboo, hard wood viz., eucalyptus, salai, agricultural residues and waste paper are supplemented (5). Thus, raw materials contain two naturally occurring most abundant polymers viz., cellulose and lignin. Water requirement for large pulp & paper mills varies and reported to be in the range of 250-440 m^3 per tonnes of paper produced (m^3/tonnes), which reduces to 200-350 m^3/tonnes in small paper mills (6). The paper mill based on wastepaper needs only 100 -150 m^3/tonnes water in paper manufacturing (7). Large quantity of wastewater in the range of 168-282 m^3/tonnes was generated from large pulp & paper mills (8), however, small paper mills discharged more wastewater (187- 338 m^3/tonnes), due to non-recovery of chemicals (9).

The paper mill under investigation is the oldest and largest in central India with an installed capacity of 0.08MTPA. In addition, about 0.0004 TPA tissue and poster paper was also manufactured in the unit. Water consumption for all operations in the industry was ranged between 32700-51400 m3d-1 thereby, generating 26300-38500 m3d-1 wastewater from various unit operations and unit processes viz., bamboo washings, chipper house, digester house, pulp washings, pulp bleaching, paper machine and, chemical recovery. Water requirement and wastewater generation at pulp & paper mill is presented in Tables 1 & 2 respectively.

Table 1 : Water Balance at Large Pulp & Paper Mill

Sr. No.	Details	Quantity, m^3/day
1.	Process	27100-40700
2.	Cooling	1800-4300
3.	Boiler	1100-1900
4.	Domestic	2700-4500
	Total	32700-51400

Source: Pulp & Paper mill

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Table 2 : Quantity of Wastewater Generation at Large Pulp & Paper Mill

Sr.No. Details of wastewater streams	Quantity m3/d
1. Chipper house & power house effluent	5000-9000 *
2. Coal ash supernatant from coal ash slurry settling ponds	2500-4500
3. Lime sludge supernatant	800-1000
4. Total Gr. Effluent received at ETP	15000-19500
5. Total Gr. III effluent received at ETP	8000-13500
6. Net effluent generation at pulp & paper mill	26300-38500

Source : Pulp & Paper Mill

* Same quantity of clarified Grade II effluent recycled to cheaper house and powerhouse

Based on contamination, the entire wastewater generated in the mill was categorized in three categories viz., Grade I, II, and III. Grade I wastewater consists mostly condensates from paper machine, turbine & evaporators and cooling water from spray pond. As this wastewater is non-contaminated, the entire quantity was being recycled into the process. Grade II wastewater comprises of effluent from stock preparation at paper machine, pilot and tissue plant, overflow from chlorination tower and hypo section from bleaching plant, wash water from chipper house, drain water from sludge filter vacuum pumps and supernatant from lime sludge ponds. Grade III wastewater comprises of washings and screening operations at pulp section and caustic extraction stage at bleach plant. The wastewater has a brown colour due to the presence of lignin from pulp processing

MATERIALS AND METHODS

Water Quality Analysis

The analytical procedure was followed according to Standard Methods (10). The wastewater analysis was conducted for various physico-chemical parameters, viz., pH suspended solids (SS), total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), nitrogen (TKN, NH4-N), chlorides, sulphates, phosphates and heavy metals.

Wastewater Treatment Plant

The schematics of the wastewater treatment plant (ETP) for Grade II effluent is depicted in Figure 1. The ETP comprised of following unit operations and unit processes:

- Bar screens
- Primary clarifier
- Aeration cum oxidation ponds
- Sludge drying beds (gravel and sand filters).

The schematic of ETP for Grade III effluent is depicted in Figure 2. The ETP comprised of the following unit operations and unit processes:

- Bar screens
- Primary clarifier
- Anaerobic lagoon
- Aeration basin
- Secondary clarifier
- Polishing pond
- Treated effluent holding pond (emergency storage)
- Sludge drying beds (gravel and filters)

Designed and observed quantity of

Table 3 : Design and Observed Wastewater Generation at Pulp & Paper Mill during Post Monsoon, Winter and Summer Seasons

Season	Wastewater Generation, $m^3 d^{-1}$							Paper Manufactured, $MT d^{-1}$	Wastewater generation, $m^3 MT d^{-1}$
	Raw Gr. II	Clarified Effluent recycled to chipper house & power house	Net Gr. II effluent	Raw Gr. III Effluent	Coal ash slurry supernatant	Lime Sludge supernatant	Total wastewater generation		
Design	20500-28500	5000-9000	15000-19500	8000-13500	2500-4500	800-1000	26800-38500	250	200
Observed									
Post Monsoon	24401	7637	16764	15223	2940	810	35737	192	186.13
Winter	25901	6603	19298	13413	2864	817	36392	187	194.60
Summer	23878	7637	16241	8629	3000	900	28770	179	160.72

Source: Pulp & Paper mill

wastewater generation along with paper production at the pulp & paper mill during post-monsoon, winter and summer seasons is presented in Table 3. All the effluents generated from various unit processes and unit operations in the mill were conveyed to two effluent treatment plants separately, designed for Grade II and Grade III effluents.

Performance evaluation

The performance of both the ETPs was evaluated for a period 10 days in post monsoon, winter and summer seasons to identify seasonal variations. An hourly flow variation in combined wastewater received at both the ETPs and combined final treated effluents discharged were monitored for a period of 10 days in three seasons. Hourly samples of wastewater at various stages of treatment from both the ETPs were collected separately over a period of 24 hours for 10 days in all seasons. The samples were flow composited and analysed for various physico-chemical parameters including heavy metals.

LABORATORY TREATABILITY STUDIES

Chemical coagulation

Bench scale treatability studies were conducted to treat effluent from secondary clarifier at Grade III ETP, to suggest improvement in the quality of treated effluent including colour removal. Phipps & Bird (USA) jar test apparatus was used during chemical coagulation experiments. Studies to optimize chemical coagulant dose were undertaken. Alum doses in various quantities ranging from 50 to 300 mg 11 with an incremental dose of 50 mg l-1 were incorporated in coagulation studies to treat secondary clarifier effluent from Grade III E T P. The admixture (effluent + alum) was subjected to flash mixing at 100 rpm for 20 seconds followed by slow mixing at 30 rpm for 25 minutes. The floc formed was allowed to settle for 60 minutes and then supernatant was carefully decanted and analysed for various physico - chemical parameters.

For removal of colour, the effluent from alum addition (200 mg l-1) was further subjected to chemical treatment using calcium hypo chlorite at various doses ranging from 15 to 60 mg l-1 with an incremental dose of 15 mg l-1 . The admixture was subjected to mixing using mechanical shaker for 10 minutes duration. The effluent from chemical treatment was analysed for various physico - chemical parameters.

Alum Recovery

Alum used in chemical coagulation treatment forms gelatinous insoluble aluminum hydroxide that settled as a flock. The sludge after decantation was then dissolved in concentrated sulphuric acid for conversion of insoluble inorganic aluminum hydroxide into soluble aluminum sulphate. The clear acidic solution after settling for insoluble sludge (impurities) was further utilized for next batch of chemical coagulation.

RESULTS AND DISCUSSIONS

An hourly flow variation at inlet of grade II and Grade III ETPs were monitored for a period of 10 days. The quantity of effluent received at Grade II was observed in the range of 18300 to 25000m^{3}d-1 with average value of 21800m^{3}d-1. And for Grade III ETP was in the range of 8000 to 13520 m^{3}d-1 with an average value of 11450 m^{3}d-1. Hourly collected and flow composited wastewater samples from Grade II & III ETPs were analyzed for various physico-chemical parameters. The characteristics of wastewater at various stages of treatment at both the ETPs along with standards for effluent discharge into inland surface waters prescribed by the regulatory agencies are presented in Tables 4 & 5 respectively. The concentration range of heavy metals at variou stages of treatment at both the ET s is given in Tables 6 and 7 respectively. The results on performance evaluation revele that treated effluent from oxidatior ponds at Grade II ETP comply wit all the standards including heavy metals, prescribed by the regulatory agencies for discharge of effluent into inland surface waters. However, the treated effluent from Grade III ETP does not comply with prescribed standards with respect to SS, COD & BOD parameters and needs further treatment for improvement in its quality. The concentration of heavy metals at both the ETPs was well within the standards prescribed by the regulatory agencies.

Mixed Liquor Suspended Solids (MLSS) concentration in the aeration basin was observed to be in the range of 2140 to 2480 mg l-1 as agains designed value of 3000mg l-1. Mix d Liquor Suspended Solids (MLV S) was in the range of 1754-2080 m l-1. Dissolved oxygen was in the ange of 0.3 to 0.8 mg l-1. Organic oading rate in aerobic system was wo ked out to be 0.28 kg m-3 d-1 as a ainst the designed value of 0.25 kg m-3 d -1. Food to microorganism atio in the aeration basin was fou d to be 0.14 kg BOD kgMLSS-1d-1 as against the designed value of 0.1 kg BOD kgMLSS-1d-1. Ther fore, the aerobic system was slight y overloaded due to poor functio ing of anaerobic lagoon because of accumulation of sludge over th years of operation. SS, COD, and BOD removal efficiency n aeration basin at Grade III ETP were found to be 31.1-39.8 %, 42.3-58.6% and 61.2-69.0% espectively. The poor perform nce of aerobic basin was due to high F/M ratio and low MLS concentrations. Low MLSS con entrations were observed as a res lt of insufficient nutrients & d solved oxygen, low sludge recycle nd presence of foam at aeration basin. Additional organic load was exerted on the aerobic system due to poor functioning of anaerobic lagoon.

Treatability Studies

Laboratory treatability studies were conducted using chemical coagulant alum at various doses for removal of colour, SS, COD and BOD from secondary clarifier effluent at

Table 4 : Characteristics of Grade II Wastewater from various Stages of Treatment at ETP during Post Monsoon, winter and summer seasons

Sr. No.	Parameters	Influent		Effluent from				Standards for Effluent Discharge onto inland Surface Water	
				Primary Clarifier		Oxidation Ponds		MEF#	MPPCB
		Avg	SD	Avg	SD	Avg	SD		
1.	Turbidity, NTU	218	40	92	24	15	6	-	-
2.	pH	7.1-8.6	-	7.0-8.5	-	7.4-8.4	-	5.5-9.0	5.5-9.0
3.	Total Alkalinity	327	76	285	75	242	84	-	-
4.	Total Suspended Solids	413	60	72	8	34	3	100	100
5.	Total Dissolved Solids	1706	59	1386	24	1134	33	-	2100
6.	Dissolved oxygen	1.0-2.0	-	1.6-2.4	-	3.2-4.1	-	-	-
7.	COD	416	58	303	47	78	12	250	250
8.	$BOD_{5d, 20°C}$	120	18	74	15	14	3	30	30
9.	Chlorides	467	40	438	32	386	38	1000	1000
10.	Sulphides	2.2	0.3	1.4	0.2	0.23	0.09	2.0	2.0
11.	Sulphates	140	16	124	8	116	9	1000	1000
12.	Phosphates	2.6	0.19	2.3	0.33	0.5	0.14	5.0	5.0
13.	Total Kjeldhal Nitrogen	5.98	0.42	5.72	0.82	4.29	0.41	100	100
14	Calcium	122	15	93	8	63	10	-	-
15	Magnesium	22.2	1.04	19.4	1.24	12.9	0.86	-	-
16	Sodium	84.5	7.1	76.8	7.2	71.0	6.3-	-	-
17	Potassium	32.3	1.2	31.0	0.9	27.7	0.6	-	-
18	Percent Sodium	29.25	0.75	31.97	2.21	33.09	2.78	60	60

All values are in mg l^{-1} except turbidity, pH and percent sodium
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Avg- Average; SD- Standard Deviation

Table 5 : Characteristics of Grade III Wastewater from various Stages of Treatment at ETP during Post Monsoon, winter and summer seasons

Sr. No.	Parameters	Influent		Effluent from										Standards for Effluent Discharge Onto Inland Surface Water	
				Primary Clarifier		Anaerobic Lagoon		Secondary Clarifier		Polishing Pond (B)		Storage Lagoon		MEF#	MPPCB
		Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD		
1.	Colour (Pt Co. Units)	2710	414	2647	415	1977	476	1179	109	1016	162	703	196	-	*
2.	pH	6.3-9.2	-	7.0-8.5	-	7.2-8.6	-	7.4-8.3	-	7.3-8.2	-	7.3-8.5	-	5.5-9.0	5.5-9.0
3.	Total Alkalinity	378	46	362	52	384	28	344	25	344	48	386	61	-	-
4.	Total Suspended Solids	362	49	148	24	183	23	133	9	120	7	110	5	100	100
5.	Total Dissolved Solids	2778	190	2684	200	2511	202	2089	123	2028	125	1982	124	-	2100
6.	COD	811	53	748	51	522	63	290	48	274	44	270	32	250	250
7.	$BOD_{5d, 20°C}$	243	13	213	13	120	9	45	5	37	4	35	4	30	30
8.	Chlorides	770	25	758	26	724	24	665	26	658	41	654	40	1000	1000
9.	Sulphides	19	2	18	2	18	2	5	1	4	1	4	1	2.0	2.0
10.	Sulphates	153	10	147	8	136	8	132	12	130	10	127	9	1000	1000
11.	Phosphates	4	1	4	1	3	0.5	1	0.2	1	0.2	0	0.2	5.0	5.0
12.	Total Kjeldhal Nitrogen	4	1	4	1	3	1	4	0.65	3	0.64	3	0.62	100	100
13.	Calcium	168	22	155	23	123	9	108	8	106	11	105	12	-	-
14.	Magnesium	15	4	14	3	11	1	9	1	8	1	8	1	-	-
15.	Sodium	247	28	241	29	217	26	194	25	190	24	187	23	-	-
16.	Potassium	35	4	35	4	32	4	30	2	30	2	29	2	-	-
17.	Percent Sodium	51	4	51	5	54	4	55	4	55	4	52	4	60	60

All values except colour and pH are in mg l^{-1} Avg- Average; SD- Standard Deviation * -Remove to the extent possible
- Gazette Notification of Ministry of Environment & Forests. MoEF. May 1993 Avg- Average; SD- Standard Deviation

Grade III ETP. Percent removal of SS, COD and BOD at various doses of alum is graphically depicted in Figure 4. The effluent from alum (200 mg l-1) treatment, complied with all the standards prescribed by the regulatory authorities. Therefore, the alum dose of 200 mg l-1 can be referred as the optimum dose. About 15 ml of concentrated sulphuric acid (99% purity or 1.835 Sp.Gr.) was required to solublize sludge completely. About 82.7% recovery of alum was thus achieved. The soluble aluminum sulphate after adjustment of pH to 6.0 can be reused in the next batch of chemical coagulation. Thus about 82% net savings towards the cost of fresh alum could be achieved. Only make-up quantity of fresh alum is need to be added in the next batch of chemical coagulation.

Addition of calcium hypo chlorite at various doses to alum treated effluent was undertaken. Dose of 30 mg l-1 calcium hypochlorite removed about 82.5% colour. Therefore, the dose of 30 mg l-1 can be treated as optimum dose of calcium hypochlorite. Percent colour removal at various doses of calcium hypochlorite from alum treated effluent is depicted in Figure 5. The quality of treated effluent improved significantly with respect to colour, SS, COD and BOD parameters.

Performance Evaluation of Modified ETP

After removal of sludge from anaerobic lagoon and also on incorporating the modifications based on laboratory treatability and pilot plant studies at aerobic biological units of Grade III ETP, the performance of modified ETP was undertaken. The characteristic of effluents at various stages of treatment is given in Table 9. The results indicated that the quality of treated effluent from modified Grade III ETP improved significantly. Insignificant colour was imparted to the treated effluent, which did not exhibit any adverse impact on surface water bodies after discharge.

CONCLUSIONS

The management in a pulp & paper mill is a continuous process where the treated effluent from ETP should continuously comply with the effluent discharge standards prescribed by the regulatory agencies. Grade I effluent was already recycled and reused in the process. Effluent treatment facilities for Grade II wastewater were adequate & efficient and no modifications were required. The treated effluent from Grade II ETP should be recycled in various processes at the mill, viz., bamboo washings, chipper house, and pulp preparation cum bleaching section.

Based on laboratory treatability and pilot plant studies, addition of 200 mg l-1 alum followed by 30 mg l-1 calcium hypo chlorite into the effluent from secondary clarifier at Grade III ETP, resulted in significant improvement in the quality of treated effluent. Implementation of suggested modifications at Grade III ETP, viz., alum dosing unit, clarifloculator followed by hypo chlorite addition with mixing units at Grade III ETP, the quality of treated effluent improved significantly to comply with the effluent discharge standards prescribed by the regulatory authorities for discharge of effluent into inland surface waters. The colour of treated effluent was reduced significantly and did not exhibit any adverse impact on surface water bodies after discharge.

ACKNOWLEDGEMENTS

The authors are thankful to the Director, National Environmental Engineering Research Institute, Nagpur for providing constant encouragement and guidance during studies. Our thanks are also due to the management of M/s Orient Paper Mills, Amalai, Dist. Shahadole, M.P.

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Table 6 : Concentration Range of Heavy Metals in Grade II Wastewater at various Stages of Effluent Treatment during Post Monsoon, Winter and Summer Seasons

Heavy Metals	Influent	Effluent from		Standards for Effluent Discharge onto land for irrigation	
		Primary Clarifier	Oxidation Ponds	MEF#	MPCB
Iron	1.258-1.786	1.164-1.404	0.310-0.586	3.0	3.0
Zinc	0.674-0.920	0.388-0.718	0.116-0.332	5.0	5.0
Lead	BDL	BDL	BDL	0.1	0.1
Nickel	0.015-0.028	0.011-0.026	0.004-0.014	3.0	3.0
Copper	0.092-0.136	0.076-0.109	0.019-0.052	3.0	3.0
Chromium	BDL	BDL	BDL	2.0	2.0
Manganese	1.984-2.486	1.342-1.792	0.588-0.980	2.0	2.0
Cadmium	BDL	BDL	BDL	2.0	2.0

All values are expressed in mg l^{-1} ; BDL – Below Detectable Limit ; # - Gazette Notification of Ministry of Environment & Forests, MEF, May 1993

Table 7 : Concentration Range of Heavy Metals in Grade III Wastewater at various Stages of Effluent Treatment during Post Monsoon, Winter and Summer Seasons

Heavy Metals	Influent	Effluent from					Standards for Effluent Discharge onto land for irrigation	
		Primary Clarifier	Anaerobic Lagoon	Secondary Clarifier	Polishing Pond (B)	Storage Lagoon	MEF#	MPCB
Iron	11.9-15.8	11.752-15.648	7.1-13.1	3.329-4.472	2.898-4.294	2.836-3.982	3.0	3.0
Zinc	3.056-4.265	2.894-4.128	1.723-3.51	0.864-1.580	0.774-1.447	0.708-1.44	5.0	5.0
Lead	0.004-0.019	0.003-0.02	0.001-0.016	0-0.002	BDL	BDL	0.1	0.1
Nickel	0.064-0.116	0.06-0.102	0.010-0.084	0.015-0.025	0.012-0.022	0.008-0.019	3.0	3.0
Copper	0.112-0.244	0.104-0.202	0.051-0.21	0.023-0.088	0.020-0.085	0.016-0.080	3.0	3.0
Chromium	0.038-0.078	0.03-0.068	0.02-0.058	0.007-0.026	0.005-0.023	0.002-0.018	2.0	2.0
Manganese	2.278-3.344	2.094-3.262	1.162-2.59	0.578-1.182	0.568-1.786	0.554-1.536	2.0	2.0
Cadmium	BDL	BDL	BDL	BDL	BDL	BDL	2.0	2.0

All values are expressed in mg l^{-1} ; BDL – Below Detectable Limit

- Gazette Notification of Ministry of Environment & Forests, MEF, May 1993

Table 8 : Characteristics of Grade III Wastewater from various Stages of Treatment at ETP after incorporating Suggested Modifications

Sr. No.	Parameters	Influent		Effluent from												Standards for Effluent Discharge onto inland Surface Water	
				Primary Clarifier		Anaerobic Lagoon		Secondary Clarifier*		Polishing Pond (B)		Chemical** Treatment Tank		Storage Lagoon			
		Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	MEF#	MPPCB
1.	Colour (Pt Co. Units)	2680	320	2620	350	1950	410	830	85	710	64	496	45	455	33	*	-
2.	pH	7.1-8.8	-	7.2-8.5	-	7.3-8.3	-	7.2-8.4	-	7.1-8.3	-	7.0-8.2	-	7.1-8.3	-	5.5-9.0	5.5-9.0
3.	Total Alkalinity	422	52	410	48	454	36	476	28	390	32	350	28	340	22	-	-
4.	Total Suspended Solids	396	44	164	32	212	29	82	16	70	12	64	14	58	11	100	100
5.	Total Dissolved Solids	2812	182	2704	154	2488	216	1956	150	1944	132	1928	122	1920	118	-	2100
6.	COD	850	64	782	56	490	44	264	36	258	28	240	12	238	9	250	250
7.	$BOD_{5d,\ 20°C}$	255	20	225	15	115	11	38	6	35	5	25	6	24	4	30	30
8.	Chlorides	794	38	770	32	756	44	684	28	681	25	698	29	696	24	1000	1000
9.	Sulphides	22	4	20	3	30	4	2.2	0.8	2.0	0.7	1.5	0.4	1.2	0.5	2.0	2.0
10.	Sulphates	166	18	159	14	142	12	158	16	152	14	149	11	148	10	1000	1000
11.	Phosphates	6.4	1.2	5.9	1.1	3.2	0.7	7	0.3	0.6	0.2	0.3	0.1	0.2	0.1	5.0	5.0
12.	Total Kjeldhal Nitrogen	7.2	0.8	6.9	0.6	5.1	0.5	2.2	0.6	2.1	0.4	1.9	0.3	1.8	0.3	100	100
13.	Calcium	176	27	170	24	154	18	122	14	120	12	134	16	133	11	-	-
14.	Magnesium	18	6	17	5	13	5	11	4	11	4	10	3	10	3	-	-
15.	Sodium	266	34	258	31	239	28	232	24	230	22	236	20	235	18	-	-
16.	Potassium	38	6	36	5	32	5	28	4	28	3	26	3	26	3	-	-

All values except Color & pH are mg l^{-1}

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Avg- Average; SD- Standard Deviation; *after alum addition; ** chemical-Sodium hypo chlorite