

# POLLUTION AND ITS ABATEMENT IN THE PULP & PAPER INDUSTRY

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## SUMMARY

This paper describes the characteristics and flows of individual waste waters from a bleached sulphate pulp and paper mill manufacturing about 150 tonnes paper/day. The major pollutants in pulp and paper mill wastes are suspended solids, dissolved organics and dark colour. The waste waters from Pulp Mill and Chemical Recovery section are quite different from that of Paper Machine section as shown by their physiochemical characteristics. The combined effluent from the pulp mill and chemical recovery section in addition to primary treatment which consists of removal of settleable solids, may require secondary treatment for Biochemical Oxygen Demand (BOD) reduction. If further purification of the waste waters is required a colour removal step for the caustic extraction stage effluent may also have to be included. On the contrary the paper machine effluent needs only a primary treatment. A cheap method of irrigation disposal of effluents after the primary treatment is recommended to reduce cost of treatment. The extent to which treatment has to be given should be determined by individual conditions since each condition constitute a different problem. The paper gives data on colour removal, BOD reduction, settling and physico-chemical characteristics of waste waters as obtained in the Research Laboratory and is therefore indicative of the concern of those directly or indirectly involved with the manufacturing process.

The subject of environmental control has achieved great significance in view of the moun-

ting public demand for a clean air and water. Since paper making as is mostly practiced in the country comprises reduction of the fibrous raw material viz. bamboo or hardwoods first to chips in multiknife chippers, digesting of chips with caustic soda and sodium sulphide at high temperature and pressure, washing of pulp for the recovery of chemicals, screening of pulp for the removal of shives and then further bleaching the fibres for the production of white printing and writing papers, it creates problem of environmental control. Most of the pulp paper mills in the country convert bamboo or wood into bleached paper by the above i e, sulphate process and multistage bleaching. The conversion involves the usage of the large volumes of water (400-450m<sup>3</sup>/tonne paper) in mills having very little water reuse and this water is finally let off as waste water into river streams. Since this waste water carry suspended matter, dissolved inorganic chemicals, dissolved organics, and has a colour and toxicity it contributes to water pollution. Water pollution in the sense, that water of receiving stream may become unfit, for human consumption, aquatic life etc. Pulp and Paper Mills contribute to air pollution also. The peculiar odour of reduced volatile sulphur compounds such as CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S, (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> and H<sub>2</sub>S is not uncommon in sulphate mills. Thus when considering the subject of environmental control, paper industry contribute to problems of water and air pollution and solid waste disposal. In this paper only water pollution, and further what measures are in the offing by the Pulp and Paper Industry to overcome this vital problem are discussed.

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Since much is being said about the water pollution by the pulp and paper industry, in

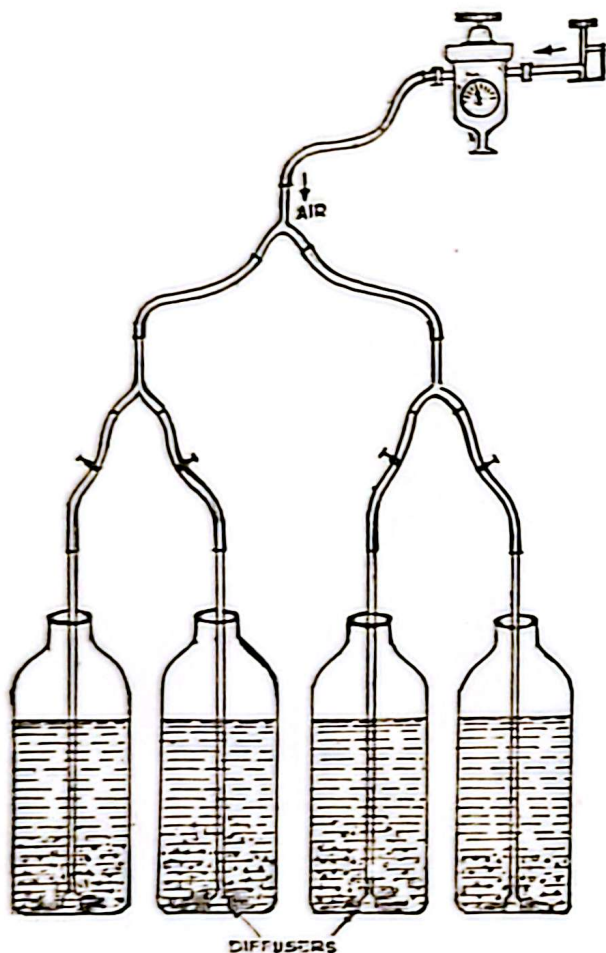
recent years efforts have been made to characterize the waste waters from different sections and also measure the volume of waste water from each section. This information is a must when considering measures to be followed, for reducing water pollution either through in plant approaches or external treatment methods. The work is carried out in the Research and Development Laboratories of various mills and assistance is also obtained from the Central Public Health and Engineering Research Institute, Nagpur. The characterisation include testing of waste waters for pH, colour, total solids, suspended solids, total volatile solids, dissolved solids, chemical oxygen demand (COD) and biochemical oxygen demand (BOD). The characteristics of some of the waste waters from a bleached sulphate mill manufacturing 150 tonnes paper per day are given in Table 1. The results in Table I show that highest BOD/tonne of paper is contributed from the effluents from the bleach section. About 55% of the total BOD/tonne of paper is contributed from the multistage bleach plant effluents. In this context it is the multistage bleach plant effluents which should receive the maximum attention when considering water pollution. To a certain extent the pollutant load from the effluents of the bleach plant in the Indian Pulp and Paper Industry is the result of peculiar development of the latter. To meet the increasing demand of paper from the existing machinery and equipment, most of the pulp and paper mills are resorting to reduced delignification of the fibrous raw materials in the digester. This results in reduced black liquor solids/tonne of pulp and therefore enables to produce more paper and at the same time process the black liquor solids through Recovery and causticizing plants designed for low production rate. This has resulted in subjecting the hard cooked unbleached pulps to strong chlorine delignification during the bleaching stages and thus aggravated the problem of pollutant load from the bleach plant effluents. Paper Industry alone is not to be blamed for this. It is a consequence of increased productivity. If the pulp and paper mills have enough chemical recovery capacity, it would be possible to carry out a strong delignification in the digester itself and this would significantly reduce the pollutant load i.e., COD and BOD & colour from the multistage bleach plant effluents.

The other aspect of water pollution of the receiving stream by the waste waters of a pulp and paper mill is the presence of suspended matter in the latter. In any treatment programme for reduced water pollution, the removal of suspended solids (Primary treatment) is the first prerequisite. Suspended solids if let off into the river affect dissolved oxygen (DO) levels, the suspended solids settle to the bottom of the river bed and exert an oxygen demand on the adjacent lower layers of inlet water which subsequently affects the oxygen concentration in the upper layers by mixing and diffusion. The decay of bottom deposits of cellulosic fibres occur over a relatively long period and largely by an aerobic bacterial action. However, the surface layer of these deposits decompose aerobically and thus draws free oxygen from the surrounding water. For this consideration the suspended solids removal/reduction is a necessity from the waste water before mixing with the receiving stream. Suspended solids removal could be accomplished by any of the four processes i. e. sedimentation, contact reaction, floatation; and filtration. Table II and III gives data for the settling characteristics of pulp Mill + Chemical Recovery and Paper Machine effluents respectively as studied in the laboratory. The plain settling tests were carried out in 1 litre measuring cylinders. The results in Table II and III show that the effectiveness of removal of suspended solids by sedimentation could be maintained high for both the Pulp Mill and Paper Machine effluents especially when the former is at acidic pH values. At the neutral pH range about 75% reduction in suspended solids from the Pulp Mill + SRP wastes requires about 2 hrs detention time and in such a situation to facilitate settling, use of coagulant may be necessary. Since the paper Machine effluent after the removal of suspended solids has very low Biochemical Oxygen Demand (BOD) it needs no further treatment.

Returning to the treatment/disposal of Pulp Mill + Chemical Recovery effluent after the suspended solids removal many alternatives can be considered. Secondary treatment comprising of Biochemical Oxygen Demand (BOD) reduction may or may not be necessary depending upon receiving stream analysis and reoxygenation capacity. Another method of disposing off the effluent from a pulp and paper mill is to use it for irrigation purposes. This could be for agricultural crops or industrial forest plantations.

Depending upon individual conditions, sometimes a treatment for BOD reduction may be required.

The treatment methods for BOD reduction most commonly employed consists of the use of lagoons, trickling filters, aerated stabilization basins and activated sludge plants. Where large land areas are not available, and a rapid BOD removal method is required, the industry prefers the use of trickling filter and activated sludge processes. In cases where land is easily available a low rate biological treatment system i. e. of extended aeration lagoons is quite common. The process has the advantage of operational adoptability, overall economy in the treatment of pulping wastes. Results of the laboratory tests carried out on a pulping wastes from a bleached sulphate pulp mill, using the principle of extended aeration are given in Table IV. For carrying out the tests a laboratory batch aeration apparatus (Figure 1) was first designed.



LABORATORY BATCH AERATION UNIT

FIGURE 1

This consisted of polythene carbuoys each of 30 litres capacity. Compressed air connection was provided to each carbuoy and the air was supplied through diffusers to provide good aeration. In order to collect as far as possible representative samples of the Pulp Mill + Chemical Recovery effluent, the following procedure was followed. About 100 litres of the effluent was collected over a period of 4 hours. This was allowed to settle for 2 hours, and the supernatant waste water was used for the aeration studies. Equal quantity i. e., 20 litres of the waste water was taken in each carbuoy. Experiments were carried out with and without the nutrients. Nutrients were added in the form of urea and ammonium phosphate. Further the effect of varying the quantity of nutrients on BOD reduction rate was also studied. A number of tests were carried out, however for the sake of simplicity the results obtained in one set are given here in Table IV.

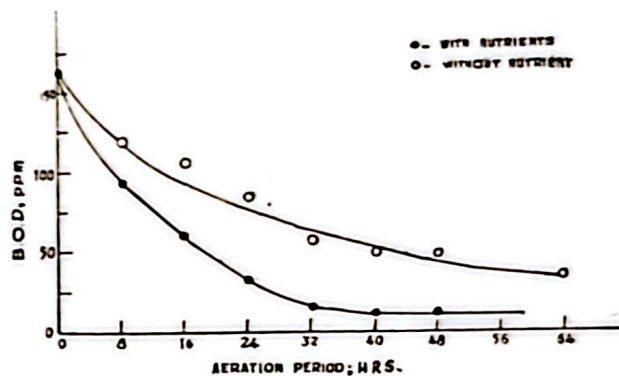


FIG 2 EFFECT OF EXTENDED PERIOD OF AERATION ON BOD REMAINING FOR PULP MILL + SQP EFFLUENT

The results in Table IV and figure 2 show that a detention time of  $1\frac{1}{2}$  to 2 days is enough to achieve 90% BOD reduction. However nutrients will have to be added to accelerate the bacterial activity and to achieve 90% and over, BOD reduction in the shortest possible time.

Another problem which is most commonly encountered in the waste waters from Pulp Mill is that of, the presence of colour. The significance of the colour in the Pulp Mill effluents is better understood today as like BOD it could also interfere with biological activity by retarding transmission of sun light into the water and is also an indication of undesirable dissolved organic chemicals. The dark colour in kraft mill effluent originates in double bonds conjugated with aromatic rings, chalcones,

quinoid structures, free radicals, metallic complexes, alkaline degradation products of sugar and chlorinated lignin derivatives. Lot of work is carried out on the reduction of colour by the use of chemicals viz. hydrated lime, alum, ferric sulphate, ferric chloride, sulphuric acid, phosphoric acid, barium alumina silicate etc. Processes based on the use of ion exchange resins, high molecular weight amines are also developed.

However, it is so far the lime treatment process which has found wider acceptance, may be because other processes are just being developed and subjected to commercial trials. While considering colour removal from kraft pulping waste, it is the caustic extraction stage waste from the bleach plant which is normally treated, since this contributes to maximum colour. In a bleached sulphate mill, the caustic extraction stage effluent have colour ranging from 7,000–12,000 pt. co. units. Treatment of this waste with slaked lime at a temperature of about 50°C for a period of 30 minutes, in quantities ranging from 2.8–3.6 g, CaO per litre of the effluent gave about 85–90% colour reduction. In addition to colour reduction there was about 44% and 61% reduction in the BOD and COD respectively. The lime sludge with the colour bodies obtained could be utilized for the recovery of CaO by reburning in a rotary lime kiln.

From the above discussion it could be inferred that when considering external treatment/disposal methods for Pulp and Paper mill waste waters there could be many alternatives. Three such alternatives are shown in fig. 3. The choice will depend upon the seriousness of the problem involved, since each situation constitutes a different problem. In some foreign mills a tertiary treatment for 91% BOD removal, and getting rid of refractory materials is also considered.

Having discussed the water pollution from a bleached sulphate pulp and paper mill, it would be befitting to discuss some of the latest trends in reducing water pollution and treatment costs. The treatment costs besides being directly related to water quality requirements and regulatory enforcement, are dependent on the volumes of waste water to be handled, for treatment. Since this could be considered, as an economic necessity, every attempt has to be made to reduce the waste water volume. This is possible through the reuse of waste volumes and many mills have been able to reduce the water consumption from 400-450 m<sup>3</sup>/tonne of paper to 225-250m<sup>3</sup>/tonne of paper. The greatest scope for reuse of water is offered by the excess white water from Paper Machine

which could be utilized after clarification on paper machine showers instead of fresh water.

Paper machine unclarified water could be supplied for direct reuse in waste paper repulping machine broke repulping, high density and low density dilution of all pulp. There is need and prospect of reducing the waste water volumes from the multistage bleach plant effluents through countercurrent washing or no washing in between some of the bleaching stages. Largest source of effluent from the bleach plant is the low consistency chlorination stage, and so far an easy way has not been found for its utilization. A few mills are utilizing a small amount of filtrate either for injection with chlorine gas or to neutralize the stock before entering the bleaching

The concept of pollution free pulp and paper mills has already gained momentum and technology is being developed. This may require adopting processes like oxygen pulping, oxygen bleaching, substituting chlorine dioxide for chlorine in the chlorination stage and completely closing up the bleaching plant effluent, high consistency or gaseous bleaching stages, sodium sulphite-oxygen pulping, improved sheet formation and paper manufacture by dry or semidry methods etc. These developments may not be of immediate interest to the Indian Pulp and Paper Industry and so the problem has to be tackled through reduced water consumption by greater recycling of filtrates, use of digester house and evaporator condensates in washing, good house keeping and irrigation disposal or simple treatment of waste waters. When considering irrigation disposal of waste waters, soil characteristics play an important part and in this respect data has to be obtained on the physical characteristics of soil, its ability to retain and transmit applied moisture, as well as the fate of organic materials added to the soil.

Further research has to be directed in developing antipollution/anticolour bleaching sequences for our raw materials and in this respect some progress(1) has been made.

#### Acknowledgement

While writing this paper references have been made to a number of very useful articles published in Tappi, PPMC, Appita, Paper Trade Journal etc., and the information obtained has been utilized here for which the authors are highly thankful.

#### Literature cited

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TABLE I

**Physico-Chemical Characteristics of Individual Wastes/Combined Waste From a Bleached Sulphate Pulp & Paper Mill Producing 150 Tonnes Paper/Day**

Source of effluent	Volume MGD	Colour	pH range	T. S. mg/l	T. V. S. mg/l	S. S. mg/l	COD mg/l	BOD <sub>5</sub> mg/l	BOD <sub>5</sub> Kgs/day	BOD Kgs/tonne of paper
1. Chipper house, chips washing unit	0.4	Brown	8.0-8.4	3064	2612	1151	1511	245	446	3.0
2. Digester house (Foul condensate)	0.1	light brown	9.2-9.4	1955	1502	42	1658	1085	247	1.6
3. Unbleached back water	1.5	brown	9.7-9.9	1601	1268	192	762	138	940	6.3
4. Chlorination stage	1.0	yellowish	1.0-1.2	1814	1385	332	1014	—	1728	11.5
5. Alkaline Extraction stage	0.5	dark brown	9.8-10.4	5712	3035	512	2966	483	1098	7.3
6. Hypochlorite stage I	1.0	Pale yellow	7.2-10.6	3650	2295	329	656	147	668	23.9
7. Chemical recovery	0.4	—	—	—	—	—	—	55	100	5.1
8. Combined effluent from Pulp Mill + Chemical Recovery	6.3	Light brown	6.8-7.3	1688	1207	440	610	184	5270	35
9. Paper Machine	4.1	whitish	4.0-5.5	1076	569	539	365	63	1185	8

T. S. = Total Solids; T. V. S. = Total Volatile Solids; S. S. = Suspended Solids

TABLE II

## Plain Settling Results For Combined Pulp Mill And Chemical Recovery Effluent

pH	Supernatant effluent tested after minutes	S. S. mg/l	%Reduction in S. S.	COD mg/l	BOD <sub>5</sub> mg/l	%Reduction in BOD
4.2	—	168	—	617	122	—
	30	47	72.0	510	116	4.9
	60	46	72.6	491	108	11.5
	120	26	84.5	479	105	13.9
3.3	—	223	—	571	98	—
	30	58	74.0	491	98	Nil
	60	55	75.3	326	91	7.1
	120	18	91.9	311	85	13.3
6.6	—	163	—	467	92	—
	30	86	47.2	376	84	8.7
	60	71	56.4	354	84	8.7
	120	44	73.0	321	82	10.9

TABLE III

## Plain Settling Results For Paper Machine Effluent

pH	Supernatant effluent tested after minutes	S. S. mg/l	%Reduction in S. S.	COD mg/l	BOD <sub>5</sub> mg/l	%Reduction in BOD
6.3	—	589	—	267	77	—
	15	41	93.1	—	—	—
	30	26	95.6	—	—	—
	45	22	96.3	—	—	—
	60	18	96.9	55	27	65
6.3	—	639	—	285	34	—
	15	25	96.1	—	—	—
	30	19	97.1	—	—	—
	45	12	98.1	—	—	—
	60	6	99.1	31	5	85
5.0	—	663	—	365	63	—
	15	37	94.4	—	—	—
	30	25	96.2	—	—	—
	45	19	97.1	—	—	—
	60	16	97.6	45	15	76

TABLE IV

**LABORATORY BATCH AERATION RESULTS ON THE  
PULPING WASTES FROM A BLEACHED SULPHATE PULP MILL**

## Effluent characteristics

Sample	pH	D. O. mg/l	BOD <sub>5</sub> mg/l	Remarks
Sample as such	5.1	3.2	184	
Supernatant	7.0	3.5	163	pH is adjusted for aeration expt

## Aeration results

Aeration period, hours	Characteristics	Without Nutrients			Nutrients added	
					BOD : N : P 100 : 2.15 : 0.43	BOD : N : P 100 : 3.1 : 0.6
8	Temp., °C	30		30	30	
	pH	7.1		7.2	7.2	
	D. O., mg/l	3.2		2.9	2.8	
	BOD <sub>7</sub> , mg/l	120		108	94	
	% BOD reduction	26		34	42	
16	Temp., °C	30		30	30	
	pH	7.2		7.3	7.3	
	D. O., mg/l	2.3		1.5	3.6	
	BOD <sub>7</sub> , mg/l	109		68	62	
	% BOD reduction	33		58	62	
24	Temp., °C	30		30	30	
	pH	7.2		7.3	7.3	
	D. O., mg/l	3.6		3.8	4.2	
	BOD <sub>7</sub> , mg/l	86		39	33	
	% BOD reduction	47		76	80	
32	Temp., °C	29		29	29	
	pH	7.2		7.5	7.5	
	D. O., mg/l	4.8		5.6	4.4	
	BOD <sub>7</sub> , mg/l	5.8		16	16	
	% BOD reduction	64		90	90	
40	Temp., °C	30.5		30.5	30.5	
	pH	7.2		7.5	7.6	
	D. O., mg/l	5.2		5.2	5.0	
	BOD <sub>7</sub> , mg/l	50		14	12	
	% BOD reduction	69		91	93	
48	Temp., °C	30		30	30	
	pH	7.2		7.5	7.6	
	D. O., mg/l	5.2		5.4	5.3	
	BOD <sub>7</sub> , mg/l	49		12	12	
	% BOD reduction	70		93	93	
64	Temp., °C	29		—	—	
	pH	7.4		—	—	
	D. O., mg/l	4.7		—	—	
	BOD <sub>7</sub> , mg/l	34		—	—	
	% BOD reduction	79		—	—	

## Treatment/disposal of pulp and paper mill Waste Waters

### Alternatives

