Effluent Treatment in a Rayon Grade Pulp Mill

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SUMMARY

In Gwalior Rayon, Mavoor, the pulp mill and staple fibre effluents are treated by clarification, bleaching, neutralisation and anaerobic and aerobic biodegradation.

The point of discharge of effluent has been shifted 7 kms. downstream where the water is saline and is not used for drinking. We have implemented several inplant control measures like recycling of backwater and changes in the cooking process to reduce the pollution load. Although the pollution load has been reduced by about 85-90%, the effluent discharged does not fully conform to the specifications set by the Kerala State Board for Prevention and Control of Water Pollution.

INTRODUCTION

Gwalior Rayon Silk Mfg (Wvg) Co. Ltd., Mavoor manufactures rayon grade pulp from all kinds of mixed hardwoods and bamboos by prehydrolysis sulphate process. In this process the properly cut wood chips are subjected to a "prehydrolysis cooking" with dilute inorganic acid (0.5–1.0 gpl). The prehydrolysed chips are then cooked by the conventional alkaline sulphate cooking. The pulp is then washed, screened, bleached by CEHEDH sequence, and made into sheets. A part of this pulp (40 tons/day) is converted to viscose staple fiber in its Staple Fibre Division and the rest is marketed as such. The factory also manufactures white and coloured paper (7-8 tons/day) from waste paper cuttings.

During pulping substantial portions (nearly 50%) of the wood in the form of hemicelluloses, lignins, tannins, resins and related compounds are removed from the pulp fibers. Of these, a part which is removed by alkaline cooking is burnt off during chemical recovery and the rest passes over into the liquid effluents.

The effluents produced at different stages exhibit marked qualitative and quantitative variations. The effluents from the prehydrolysis cooking and washing of wood chips, viz. prehydrolysate liquor and prehydrolysate wash are high in organic content COD

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and BOD. They contain mainly noncellulosic carbohydrates, resin acids, tannins and hydroxylated quinones. Average characteristics of these two effluents are listed in Table-I. Besides this acidic stream, effluents are also generated in the processes of washing, bleaching, drying, paper making and chemical recovery. They contain lignins, tannins and their degradation products insolution and suspended particles. At present these effluents which are mostly alkaline and coloured are treated together as combined effluent. The effluents from the SFD are highly acidic and are of low COD and BOD. They contain traces of zinc, xanthate decomposition products and suspended materials. The average characteristics of the different streams in the combined effluent and of the SFD effluent are given in Table-II.

PRESENT TREATMENT

The treatment now given is based on clarification, bleaching and microbial action. The effluents are segregated into three main streams, viz. prehydrolysis effluents and combined alkaline effluents of Pulp Division and the SFD effluents, for preliminary treatment. Since these three streams vary widely in nature and pollution load, the methods adopted for preliminary treatment are also different. The prehydrolysis effluents, viz. prehydrolysis liquor and wash are highly acidic and are of high COD and BOD. Hence they are neutralised with lime and subjected to anaerobic and aerobic biodegradation to reduce the organic load. The combined effluents are highly coloured and contain suspended impurities (mainly

pulp fibers). Hence these effluents are clarified to remove suspended materials and bleached with calcium hypochlorite to remove colour. The staple fiber division effluents are acidic and contain traces of zinc (from the spin bath). To remove zinc they are treated with lime to pH 7.5-8.5 and allowed to settle when zinc hydroxide precipitates down. The above three effluent streams after the respective preliminary treatment join together in a large tank in which final aeration is carried out before letting out into the River 'Chaliyar' joining the Arabian Sea.

PULP DIVISION EFFLUENTS

PREHYDROLYSATE EFFLUENTS (pH LIQUOR AND pH WASH)

Of the three streams, the one with highest pollution load (organic content) is the pH liquor and pH wash mixture. The mean COD and BOD of this stream are around 40,000 and 20,000 mg/l respectively. This being too high an organic load for effective aerobic biodegradation, the pH effluents are first subjected to anaerobic treatment. The anaerobic treatment is done by lagooning. The pH and temperature of the effluent have to be adjusted for optimum bacterial action. For this the effluent is treated with lime slurry (2-3%) to pH 7.0-7.5. On settling for about 2 hours, 7% V/V sludge consisting mainly of calcium sulphate and traces of calcium salts of resin acids gets deposited in a settling tank. The overflow from the settling tank is cooled to a temperature of 35-40 °C in a cooling tank equipped with a cascade cooling arrangement. The cooled effluent (BOD about 20,000 mg/l) is then fed into the anaerobic lagoons.

There are 3 anaerobic lagoons, 2-3 metres deep and with total capacity of 45,000 M³. With pH effluent volume ranging from 1500-1800 M3/day, a detention time of 25-30 days is available. The three lagoons can be charged in series or in parallel. The lagoons are initially innoculated with accimalised cowdung which serves as the bacterial source. Diammonium phosphate and urea are added according to the ralation BOD : N:P-100:2.5:0.5 to provide nutrients necessary for sustaining bacterial action as per pilot plant studies on microbial treatment carried out by scientists from NEERI(1,2). In the lagoon, excepting at the surface (where aerobic processes may set in) anaerobic decomposition of the organic compounds takes place. It is envisaged that several combinations of anaerobic bacteria operate, converting the organics first into volatile aliphatic acid and finally into methane and carbon dioxide. Generally the acid forming (saprophytic) bacteria considerably out number the methane formers. The methane formers are more sensitive to changes in conditions like pH, temperature and organic load. Adverse changes in these conditions will tend to eliminate the

methane formers and eventually result in increase in acid concentration (souring) in the lagoon. An increase in volatile acid concentration in the lagoon (above 500 mg/l) indicates this condition which causes fall in anaerobic reaction rate and thus lagoon failure. For effective anaerobic stabilization of the effluent, proper balance between acid formers and methane formers is to be ensured by keeping constant vigil on pH, temperature, load and volatile acids. With a BOD load of 0.5-0.8 kg/M³/day and detention time of 25-30 days we have been able to get about 80-90 % reduction in BOD by anaerobic treatment.

The effluent after anaerobic treatment has still high BOD of 5000 mg/l and COD of 12,000 mg/l. This is then treated in two aerobic lagoons which are charged in series. Each lagoon is equipped with six numbers of fixed surface aerators (low RPM 20 HP). These two lagoons with a total capacity of 17,000 M³ provide a detention time of around 10 days. These aerobic lagoons function at a low MLVSS concentration of around 500 mg/l and do not require any sludge return. They afford 50-60% reduction in BOD at a relatively low cost. The overflow from the second aerobic lagoon has a BOD of around 2500 mg/l and COD of around 6500 mg/l and is taken into a large lagoon equipped with 24 numbers of aerators (24 aerator lagoon) for final treatment.

COMBINED EFFLUENT

The second stream, viz. the combined effluent is highly coloured (colour around 2000 Co/Pt units), but is of low COD (1200 mg/l) and BOD (500 mg/l). It also contains suspended impurities which include coarse wood wastes and pulp fibers. The coarse materials settle down on passing through a detritus tank.

The overflow from the detritus tank has a TSS of 200 mg/l which is removed in a Dorr Oliver Clarifier (160' \times 12'). The sludge removed consisting mainly of pulp fibers is pumped into drying beds. This waste pulp is being tried for paper and board manufacture. The overflow from the clarifier although nearly free from suspended particles, is still highly coloured. For removing its colour, we have tried several methods like massive lime treatment, alum treatment, ferric chloride/lime treatment, charcoal adsorption and calcium hypochlorite bleaching. Of all these, the most feasible method was found to be calcium hypochlorite treatment. 15-20 gpl calcium hypochlorite prepared in the plant itself from lime slurry (2-3%) and chlorine is used for bleaching. For satisfactory decolourisation about 200 mg of elemental chlorine is needed per litre of the combined effluent. The colour flocs formed on mixing the clarifer overflow with calcium hypochlorite slurry are allowed to settle in two stabilization lagoons which are connected in series. These two lagoons with a total capacity

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TABLE—I. VOLUMES AND ANALYTICAL CHARACTERISTICS OF PREHYDROLYSATE EFFLUENTS

Effluent	Flow M ³ /day	рН	TS mg/l	TSS mg/l	Colour Co/Pt Units	COD mg/l	BOD mg/l
pH liquor	750	3 – 4	62,000	1000	8000	61,000	25,000
pH Wash	900	3.5-4.5	30,000	550	4000	38,000	15,000

TABLE—II. VOLUMES AND ANALYTICAL CHARACTERISTICS OF INDIVIDUAL DRAINS OF COMBINED EFFLUENT AND SFD EFFLUENT

Effluent	Flow M³/day	рН	TS mg/l	TSS mg/l	Colour Co/Pt Units	COD mg/l	BOD mg/l
**7 1'		0.10	1700	100	.	1000	65 0
Washing	2000	910	1700	100	2400	1200	350
Bleaching	5000	8-9	2400	200	1500	550	80
Wet End	100	3-4	800	200	105	75	50
Paper Plant	1500	4-5	2100	1000	100	110	70
Evaporator	8500	9-11	3000	150	2000	1500	450
Chipper	2000	6.5-7.0	250	150	100	50	5
Causticizing and Lime-kiln	3000	9-10	3600	2700	200	- 150	50
SFD	7000	3-5	—	300	Wite and	550	150

TABLE—III. ANALYTICAL CHARACTERISTICS OF EFFLUENTS AT VARIOUS STAGES OF TREATMENT

Effluent	pH	Colour Co/Pt units	COD mg/l	Reduction %	BOD mg/l	Reduction %	
Cooling tank inlet	7–8	7000	45,000		24,000		
Anaerobic outlet	7–8	6200	12,000	73	5,000	80	
Aerobic outlet	7–8	6500	6,500	46	2,500	50	
Clarifier inlet	7–9	2000	1,100		500		
Clarifier outlet	7–9	1600	900	18	450	10	
Stabilization lagoon outlet	8-10	800	850	5	400	11	
SFD inlet	35	·	550	·	150		
SFD outlet	7.5-9.5		450	18	100	33	
24 aerator inlet	7.5-8.5	1200	1050		450		
24 aerator outlet	7.5-8.5	1000	500	53	200	56	

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of 36,000 M^3 provide a detention time of 18 hours for sedimentation of the colour flocs. The overflow from the stabilization lagoons has a colour of around 800 Co/Pt units and BOD of around 400 mg/l. This then mixes with the treated pH effluents in the 24 aerator lagoon for final treatment.

STAPLE FIBER DIVISION EFFLUENT

The third stream, the effluent from the Staple Fiber Division is acidic and is of low COD (550 mg/l) and BOD (150 mg/l), but contains about 1-5 mg/l of zinc. This effluents is treated with lime to bring up the pH to 7.5 - 8.5 and allowed to settle in a stabilization lagoon. During 24 hours settling in this lagoons of capacity 7900 M³, the zinc hydroxide and suspended fibrous materials settle down. The overflow enters the 24 aerator lagoon for aeration.

FINAL TREATMENT OF PULP & STAPLE FIBER EFFLÜENTS

All the three effluent streams, viz. prehydrolysis, combined and SFD effluents get mixed together in the 24 aerator lagoon. This admixture with a BOD of around 450 mg/l is subjected to aerobic treatment in the 1,75,000 M³ capacity lagoon which provides a detention time of 5-6 days. Aeration is done with the help of 24 numbers of fixed low RPM surface aerators (20 HP). The system works with 50-60% efficiency at a MLVSS concentration of 400 mg/l (food to microbe ratio of 0.9-1.1).

DISPOSAL OF TREATED EFFLUENT

The overflow from the 24 aerator lagoon has a BOD of 200 mg/l COD of 500 mg/l and colour of 1000 Co/Pt units. This effluent is discharged into the Chaliyar river. Chaliyar has a minimum flow of 150 cusecs in the peak summer, so that the effluent is nearly 10 times diluted. During the monsoon months the flow in the river is several thousand cusecs. Till recently the treated effluent used to be discharged about 1.6 km down stream from the factory. Now to avoid any possible contamination of the drinking water by effluent carry over during high tides, we have just commissioned a project for pumping the treated effluent by pipe line to point 7 km down stream. At this point the water is saline and even during high tides the effluent discharged here does not reach the drinking water. The total capital investment for the effluent treatment and disposal project has come to around Rs. two crores.

INPLANT CONTROL MEASURES

In 1963, when the pulp and paper mill started production, the total water consumption was around 50,000 M^3 per day. This quantity was reduced to

about 35,000 M³/day by 1977 and now it has been brought down to about 25,000 M³/day.

This reduction in water consumption and hence in the quantity of effluent let out has been achieved by careful control and reuse of water.

In order to reduce fresh water consumption and effluent load pulp washing is being done in a closed cycle with practically very little use of fresh water. Chlorine, 2nd alkali and 2nd hypo back waters have found reuse in washing, 1st alkali and ClO_2 stages respectively. Similarly, in washing, bleaching, Wet End and causticizing fresh water has been partially or completely replaced with recycled warm water from the boiler and recovery section. White water is completely conserved and fully utilized. By adopting these water recycling measures and practicing greater economy in every department we have been able to bring down the effluent volume by nearly 12,000 M³/day.

Possible reuse of about $3,000 \text{ M}^3$ of combined effluent in log washing in the chipper house and shell washing in the lime kiln is being examined. Also installation of a "Save all" in paper plant to recover fibers and suspended particles from paper machine back water is expected to provide about $1,000 \text{ M}^3$ of reusable white water and reduce the suspended solids in the effluent. Other possibilities of water recycling are also being explored. We have studied and introduced various changes in cooking and bleaching to bring down the effluent load.

PROBLEMS ENCOUNTERED

Following are some of the difficulties that we meet with in the present treatment system :

1. SLUDGE REMOVAL

Large quantities (7-9 tonnes/day) of lime sludge are formed during neutralisation of pH effluents and SFD effluents and during hypochlorite bleaching of combined effluent. At present this sludge is allowed to settle in either settling tank or stablization lagoons and periodically removed manually. This procedure is time taking and cumbersome. Another clarifier is being constructed to tackle the hypo treatment sludge. We are keenly interested to find out a process by which we can avoid formation of such large quantities of sludge.

2. FOAM

The phenolic resin acids in the pH effluents and the phenolic lignin degration products in the combined effluent generate large amounts of foam in the lagoons. The foam when it gets dry, starts flying in the air and is a source of aesthetic nuisance, if not a health

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hazard. The foaming is greater in the aerobic lagoons due to agitation of the surface water. We have brought this foam under control by arranging aereal sprinklers all around the aerators.

3. COLOUR REMOVAL

Though in the present treatment method the combined effluent is bleached with calcium hypochlorite, it has not been possible to decolourise it completely. Use of excess of hypo is ruled out since it will increase the residual chlorine level in the effluent. Also it has been found practically impossible to decolourise the pH effluents (average colour 6000 Co-Pt units) which is resistant to all types of colour removal methods.

The effluent that is now discharged after treatment from this factory has a pH of 7.5-8.5%, TSS of 40-60 mg/l COD of 400-500 mg/l, BOD of 175-200 mg/l and colour of 1000-1200 Co/Pt units. Out of these the COD and BOD values are above the TLV prescribed by the Kerala State Board for Prevention and Control of Water Pollution. In this context it has to be said that the TLV fixed should be more realistic taking into consideration the socio-economic

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problems of the state, the geographic and topographic conditions of the region and the effective concentration of the pollutants in the receiving waters. However, we are aware of the hazards of pollution and hence no efforts are spared in minimizing the quantity of effluent, brining down the pollution load and thus preserving the plant and aquatic life of the region. Also, we have approached Scientists and Technologists of various universities and several consultants in Environmental studies for more technical know-how in giving better treatment to the effluents.

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