Combined Chemical-biological Treatment of Pulp and Paper Mill Effluent

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ABSTRACT

Most of the pulp and paper industries in India are expanding their production capacity to cope-up the increasing demand of paper and paper board with the same or marginally higher water permit. The industries are facing the task of handling the increased organic load and pollutants concentration in the effluent which is treated in the existing or partially modified plant. The recycling of wastewater is also dependent upon the removal of pollutants to a great extent. A low sludge bioprocess (LSB), where sludge and hydraulic retention times are same has been studied for treatment of pulp mill effluent along with post chemical treatment. Chemical pretreatment of specific streams containing high pollution load was found techno-economical instead of the above treatment on combined effluent. Although the performance of LSB was a little inferior to that of activated sludge process (ASP), it was possible to treat the treated wastewater from the LSB through post chemical treatment. Intermediate settling is not required unlike ASP, as LSB is operated without recycling of sludge. The separation of combined sludge can be performed in the secondary clarifier. The concentration of COD in the pre and post biologically treated wastewater in LSB was 754±28 and 337±39 mg/l respectively. The concentration of colour in the wastewater was 1676±134 Pt-Co unit and about 27±5.4% removal of colour was observed in the biological treatment. After post chemical treatment unclarified wastewater of LSB, the COD and colour were 133 mg/l and 280 Pt-Co unit respectively. The variable treatment cost was only Rs. 2.0±0.2 /m^3 of the effluent generated. The chemical treatment also resulted in lower total dissolved solids in the treated wastewater.

Keywords: *Activated sludge process, COD, Colour, Coagulant, Flocculant, Low sludge bioprocess*

Introduction:

The pulp and paper manufacturing is one of the core industrial sectors in India and plays a vital role in socio-economic development, while it is associated with significant environmental concerns due to its large footprints on environmental resources. Due to relatively old process technology, considerable quantity of water is used in papermaking processes and the quantity of water consumption varies according to quality and kind of paper to be manufactured (MOEF, 2010; Shaw and Lee, 2009). Most of the pulp and paper industries in India are expanding their production capacity to cope-up with the increasing demand of paper and paperboard with the same or marginally higher water permit. The quality of raw water is deteriorating as well as its availability is continuously diminishing; on the other hand demand for domestic use is increasing. The socio-economic factors are forcing the industries to recycle the maximum of its wastewater. The pretreatment of organic rich wastewater to a considerable degree is prerequisite for recycling of wastewater as such or after other treatments. The stage wise sources of wastewater and generation of pollutants in an integrated pulp and paper mill are given in Table 1.

Biological oxidation process particularly activated sludge process is well adapted and proven for treatment of the pulp and paper mill effluent. Significant portion of the biodegradable components is removed with this process. Pulp mill effluents contain noticeable amount of compounds that are recalcitrant to the biological treatment (Bijan and Mohseni, 2004). The recycling of inefficiently treated wastewater may cause slime growth, scum and scale formation (Pokhrel and Viraraghavan, 2004).

The present study is aimed at comparing the efficacy of pre-chemical treatment of individual and combined raw wastewater, performance evaluation of activated sludge process with low sludge bioprocess with no recycling of biosludge followed by chemical treatment.

Materials and Methods

Source of seed sludge and wastewater

The secondary sludge samples were collected from an effluent treatment plant (ETP) of an integrated kraft pulp and paper mill in North India based on $C_D E_{OP} D_1 D_2$ bleaching sequence. The seed sludge was generated by mixing screened cow-dung and secondary sludge in 50:50 ratio of MLVSS. Wastewaters from partially chlorine dioxide substituted chlorination (C_D) and alkaline extraction (E_{OP}) stages were collected which were the major sources of pollution generation especially of COD, colour and AOX. The other stream that also contributed to COD and colour was spillage of black liquor from pulp mill and chemical recovery section; weak black liquor (WBL) of 16-17% solid concentration was also collected to simulate the contribution of black liquor spillage in wastewater.

Reactors for lab scale activated sludge process

Two laboratory scale reactors with volume capacity of 9.5 liter each were used as aeration tank, followed with two settlers in series with 4.0 liter volume of each. Urea and technical grade phosphoric acid were used as the source of nitrogen and phosphorous and were fed based on soluble COD (CODs) removal: N: P::100: 5: 1 with separate peristaltic pumps. The C_D and E_{OP} streams were mixed in 2:1 ratio and WBL was added to the blend of C_D and E_{OP} wastewaters to adjust the CODs and AOX concentration for the feed to bioreactors. Starch solution was also added to simulate the wastewater characteristics from integrated pulp and paper mill. The pH of the resulting wastewater was adjusted to 7.0 and filtered through high porosity filter paper (70 µm) to remove coarse particles. The filtrate was used as the substrate for feeding into the activated sludge reactors. The substrate was fed into reactors continuously with peristaltic pumps (Cole Parmer, USA). The above wastewaters and WBL were periodically collected from the mill and stored in the refrigerated condition at 4-5 ^{0}C. In case of activated sludge process, the sludge from the clarifier was recycled to aeration tank continuously with peristaltic pump and in case of low sludge bioprocess (LSB), no sludge was recycled in the biological system.

Characterization of biosludge and supernatant material

For mixed liquor suspended solids (MLSS) and MLVSS, 50-100 ml of mixed sludge sample was centrifuged, washed with distilled water for removal of dissolved solids and again centrifuged before transferring to pre-weighed silica crucible. The sample was oven dried at 105 ^{0}C for overnight. Dried material was taken as MLSS, the same crucible was ignited at 550 ^{0}C and loss on ignition was taken as MLVSS. pH, colour, COD of samples were determined as per Standard Methods (Greenberg et al., 1992). Concentration of AOX compounds of liquid sample was estimated as per ISO 9562, 1989. Morphology of organisms was characterized with image analyzer (Model Axio Scope A1, Carl Zeiss).

Coagulation and flocculation experiments

The known volume of wastewater (250-1000 ml) was agitated at 500 rpm on magnetic stirrer and treated with coagulant followed by flocculant; flocculation was performed at 50-100 rpm for 2-3 minutes.

Results and discussion

Pre-treatment of wastewater

The wastewater form pulp and paper mill contains refractory organic compounds that are hard to biodegrade during biological treatment. The pre-chemical treatment of wastewater by coagulation and flocculation is a well-established technology, suitable for pulp and paper mill wastewater containing large amounts of colloids and dissolved compounds (Verenich et al., 2001). Up to 30% of the released colour arising from bleached kraft pulp and paper production comes from the alkaline extraction stage (Joss et al., 2007). This waste stream can, therefore, be readily targeted to remove colour at source in mills where improved colour management is required. The characteristics of the wastewater from a typical bleach plant are given in table 2.

The wastewater from alkali extraction stage contributed approximately 18-20% of the volume to combined bleached plant wastewater whereas, it attributed 42-44% of colour and 23-25% of COD to the combined bleach plant wastewater. The combined bleach plant as well as E_{OP} stage wastewater were treated with varying dosage of coagulant and flocculant (Table

Table 1: Potential water pollutants from pulp and paper processes

Source	Characteristics
Wood handling/debarking and chip washing	Solids, BOD, COD, color
Chip digester and liquor evaporator condensate	Concentrated BOD, COD, colour and reduced sulfur compounds
White waters from pulp screening, thickening, and cleaning	Large volume of water with suspended solids, BOD and COD
Bleach plant washer filtrates	BOD, COD, color and chlorinated organic compounds
Paper machine back-water	Solids
Fiber and liquor spills	Solids, BOD, COD and color

Source: US EPA, 2002

Table 2: Characteristics of wastewater in typical mill for pre-chemical treatment

Wastewater	COD (mg/l)	Colour (Pt-Co unit)	Charge (meq/l)
Combined bleach plant	1471	2024	(-) 448
C_D stage	1107	1012	(-) 142
E_{OP} stage	1521	3234	(-) 2891

Table 3: Chemical treatment of concentrated stream and combined wastewater

Wastewater	Inorganic coagulant-I (g/l)	Flocculant (mg/l)	Reduction in colour (%)	Charge (meq/l)	Reduction in COD (%)	Cost (Rs/m^3)
Combined bleach plant	0.5	2.0	3	(-) 295	15	4.3
E_{OP} stage	1.9	2.0	83	(-) 894	73	15.7

3). In case of combined wastewater, reduction in colour and COD was 3 and 15% respectively at a cost of chemical of Rs. 4.3/m^3 for bleach plant wastewater. Considering the wastewater from other operations the cost may vary between Rs. 1.8-2.2/m^3 of total wastewater. Whereas, in E_{OP} stage wastewater the reduction in colour and COD was 83 and 73% respectively which corresponds to 21-24% of colour and 16-18 % of COD of the combined bleach plant wastewater. Based on the whole effluent, the cost may vary between Rs. 1.3-1.5/m^3 of total wastewater. The results revealed that the chemical treatment of highly concentrated stream is economical instead of treatment of combined diluted wastewater. The coagulation and flocculation treatment was dependent on neutralization of dissolved charge by the cationic coagulant. In case of combined bleach plant wastewater, only 34% of charge was neutralized whereas in case of E_{OP} stage wastewater 69% of charge was neutralized which resulted in higher removal of colour and COD with similar or low dosage of chemicals.

Biological treatment of pulp and paper effluent

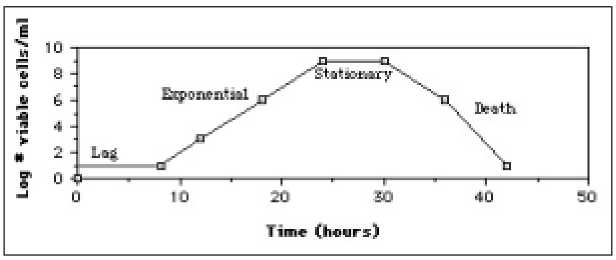

Figure 1: Bacterial growth curve showing the four stages of growth versus time

For biological treatment of wastewater, one reactor was run as conventional activated sludge process whereas, the other one was low sludge bioprocess (LSB). In LSB, no biomass was recycled to maintain the concentration of biomass in the aeration basin; hydraulic retention time (HRT) was equivalent to sludge retention time (SRT). The retention time in the reactor was optimized based on the growth cycle of microorganisms. Bacterial growth is linked with the division of one bacterium into two daughter cells in a process called binary fission. It is divided into four main phases i.e., lag, log, stationary and decline phase (Figure 1). The initial lag phase

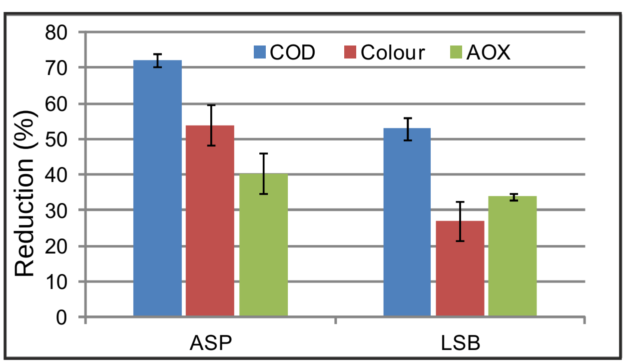

Figure 2: Performance of ASP and LSB in term of removal of COD, Colour and AOX

is a period of slow growth during which the bacteria are adapting to the conditions in the fresh medium. This is followed by a log phase during which growth is exponential, doubling every replication cycle. Stationary phase occurs when the nutrients become limiting and the rate of multiplication equals the rate of death. Logarithmic decline or death phase occurs when cells die faster than they are replaced. The HRT in LSB process should be more than the log phase to ensure the reproduction of organisms in the system. The similar process was studied by Lee and Welander, 1996 for minimizing the biosludge generation during biological treatment of pulp and paper mill wastewater.

During biological treatment in ASP and LSB the hydraulic retention time was maintained at 12-13 h. The biomass concentration (MLVSS) in ASP was 3.65±0.19 g/l whereas, the TSS concentration in LSB was 218±65 mg/l only. The TSS concentration in the process represented the biomass growth. The outlet pH of the wastewater from ASP and LSB was

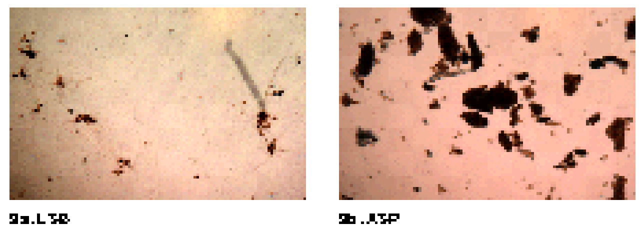

Figure 3: Morphology of biomass from LSB and ASP processes

7.8±0.3 and 8.0±0.2 respectively (Table 4). The reduction in COD in ASP and LSB were 72.1±2.0 and 53.0±3.1% respectively. Similarly reduction in colour and AOX was lower in LSB (Figure 2). The flocs were very compact in nature and higher organisms like rotifer and protozoa were present in good amount in ASP whereas, the biomass was diffused in nature in LSB (Figure 3).

Post treatment of wastewater

In case of ASP, the wastewater after secondary clarifier, and wastewater from LSB without settling, was taken for chemical treatment. The samples were treated with cationic inorganic coagulants to neutralize the anionic thrash of wastewater followed by flocculation with anionic flocculant (Table 5). At lower dosage of coagulant, the removal of colour and COD was not proportional with the dosage of coagulant. The initial charge of wastewater before biological treatment was 501 meq/l. The same was 282 and 398 meq/l in the treated wastewater after ASP and LSB treatment. The COD and colour in the post ASP treatment were 281 mg/l and 690 Pt-Co units respectively whereas, the same were 352 mg/l and 1020 Pt-Co

Table 5: Post treatment of biologically treated wastewater by ASP and LSB

Sample	Inorganic coagulant-I (g/l)	Inorganic coagulant-II (g/l)	COD (mg/l)	Colour (Pt-Co unit)	Cost (Rs/m^3)
ASP treated	0.16	0.2	94	200	2.2
	-	0.4	63	90	1.8
LSB treated	0.16	0.2	180	370	2.2
	-	0.4	133	280	1.8

Flocculant dosage: 0.5 mg/l

unit respectively in LSB. The efficacy of chemical treatment was better with wastewater from activated sludge process due to lower charge after biological treatment. The COD and colour reduction in case of ASP wastewater was 67-78 and 71-87% respectively whereas, the same was 49-62 and 64-73% respectively for the wastewater from LSB process at the same chemical dosage (Table 5). The handling of the biosludge with chemical sludge in a single clarifier was the advantage of LSB process. The rate of settling of the flocs with biosludge was comparable with that of activated sludge process.

Conclusion

Pre-chemical treatment of wastewater in concentrated form is economical instead of treatment of diluted combined wastewater. The removal of pollutants require a threshold neutralization of charge with coagulant before flocculation. Biological treatment coupled with post chemical treatment in both activated sludge and low sludge bioprocess can remove significant amount of organic pollutants. The biological treatment of wastewater with low sludge bioprocess was effective in combination of post chemical treatment and the biosludge as well as chemical sludge can be handled in a single clarifier.

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