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Biochemical abatement of pollution load in wastewater to meet the future stringent norms for agro based pulp and paper mills

Sponsored by

Indian Agro & Recycled Paper Mills Association

AVANTHA

Avantha Centre for Industrial Research & Development,
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In Collaboration with

Central Pulp & Paper Research Institute,
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Contents

Nomenclature

ACIRD	:	Avantha Centre for Industrial Research & Development
AOP	:	Advanced oxidation process
AOX	:	Adsorbable organic halides
ASP	:	Activated sludge process
ASP_{F1}	:	ASP treated wastewater fed with feed F1
ASP_{F2}	:	ASP treated wastewater fed with feed F2
ASP_{F3}	:	ASP treated wastewater fed with feed F3
BOD	:	Biochemical oxygen demand
COD	:	Chemical oxygen demand
CPPRI	:	Central Pulp and Paper Research Institute
DO	:	Dissolved oxygen
F1	:	Inlet mixed feed (7 parts of mill wastewater and 3 parts of un-treated WWAA) to ASP_{F1}
F2	:	Inlet mixed feed (7 parts of mill wastewater and 3 parts of pre-treated WWAA with alum)to ASP_{F2}
F3	:	Inlet mixed feed (7 parts of mill wastewater and 3 parts of pre-treated WWAA with PAC) to ASP_{F3}
FDE	:	Final discharge effluent
HRT	:	Hydraulic retention time
MLSS	:	Mixed liquor suspended solids
MLVSS	:	Mixed liquor volatile suspended solids
O/F		Over Flow
OD	:	Oven dried
PAC	:	Poly-aluminium chloride
PCP	:	Penta-chlorophenol
ROM	:	Recalcitrant organic matter
SAR	:	Sodium adsorption ratio
TDS	:	Total dissolved solids
TSS	:	Total suspended solids
VOCs		Volatile organic compounds
WWAA	:	Wet washing after anaerobic treatment

1. EXECUTIVE SUMMARY

The wastewater generated from pulp and paper manufacturing sector contains complex recalcitrant compounds. These compounds are hard to biodegrade in nature due to its high toxicity level. Proposed stringent norms for wastewater from pulp and paper mills have put a lot of pressure on this sector. Activated sludge process (ASP), is a widely used process in wastewater treatment of the pulp and paper industry. A considerable portion of the biodegradable materials is removed during biodegradation process in ASP, and recalcitrant portion of ASP treated wastewater is generally represented by residual colour, chemical oxygen demand (COD) and adsorbable organic halogen (AOX). There is a fundamental requirement of immediate attention to develop techno-economical solution in treatment process of wastewater generated from pulp and paper mills in India.

To meet the stringent discharge norms for treated wastewater of agro-based pulp and paper mills, various coagulants along with flocculant, enzymes and microbial consortia were applied to improve the efficiency of biological treatment. Coagulants were tried for the pre and post-ASP treatment. A positive impact on performance of ASP was found by reducing the initial load of COD and colour of highly polluted steam i.e. wastewater after anaerobic treatment (WWAA). The optimized dose of PAC was split into 2 stages. Firstly, 0.3% PAC was introduced before ASP to reduce the initial load on ASP and secondly 0.1% PAC was introduced after ASP to remove the residual recalcitrant compounds. Pretreatment of WWAA followed by ASP and post-treatment (using PAC) resulted in final discharge within the discharge norms (except TDS).The chemical sludge generated after pre and post–treatment was mixed with saw dust to form briquettes. The combustion characteristics of chemical sludge (GCV: 2013 kcal/kg) were found to be good after mixing with saw dust (GCV: 4518 kcal/kg).

Based on the results, a pilot scale (wastewater treatment capacity of 1.15 m^3/day) trial was demonstrated in an agro based pulp and paper mill. The result of various parameters were comparable as observed in lab scale trial even after using ~20% less amount of PAC.

2. BACKGROUND

The pulp & paper manufacturers have been pressurized mandatory to switch from the conventional wastewater treatment techniques to more refined ones that allow them to meet the current environmental standards. Therefore, the search for environment friendly and cost-efficient techniques for the pulp & paper industry wastewater treatment is still a severe problem. The Physicochemical treatment techniques are sedimentation through chemical or without chemical, coagulation and flocculation, adsorption by using suitable adsorbent, chemical oxidation and ultra filtration or membrane filtration.

Among these physicochemical methods coagulation and flocculation are the most widely used separation technique. The heavy particles were easily separated in filtration, sedimentation techniques without chemical addition. This coagulation and flocculation technique is based on the charge neutralization of waste water and allows them to remove. This process used in primary treatment to separate out the suspended particles. These suspended particles contribute in the total suspended solid count, BOD and COD also.

Some heavy particles are not settled down without chemical treatment. The chemical treatment is necessary to settle down the organic matter also. Sedimentation using chemical coagulation has been implied mainly to pretreatment of industrial wastewaters. The use of chemical coagulating agents to enhance the removal of BOD and suspended solids has been used extensively on industrial wastewaters, since it is not usually operationally desirable. However, special applications may exist at some installations for reduction of organic load of selective individual stream.

The increase in solids separation in primary sedimentation triggers so many positive impacts on biological system by means decrease in organic loading to secondary treatment process system. This directly enhances the degradability of organic material and a decrease in quantity of secondary sludge.

The wastewater treated from primary treatment introduced into the biological treatment process is also known as secondary treatment process or Activated sludge process. The introduction of this simple technique as pre treatment prior to biological treatment becomes more valuable than any other techniques. The Primary treatment is not acceptable alone as the total wastewater treatment should be processed through biological treatment prior to discharge to a recipient body of water so the biological treatment must be employed to meet regulatory criteria.

There are many alternative biological systems in use and each uses biological activity in different manners to accomplish treatment. Biological processes are classified by the oxygen dependence. In aerobic processes, waste is stabilized by aerobic and facultative microorganisms but in anaerobic processes, anaerobic and facultative microorganisms are present. Suspended growth processes refer to the treatment systems where microorganisms and wastewaters are contained in a reactor. Oxygen is introduced to the reactor allowing the biological activity to take place. Examples of suspended growth processes include ponds, lagoons and activated sludge systems. Now a day's activated sludge processes is widely used as biological treatment processes.

Activated sludge is an efficient process and meets remarkable COD and BOD reductions. In recent years, this process has undergone considerable changes and improvements from the conventional activated sludge process. The most important factors which control the design and function of activated sludge processes are:

- MLSS, MLVSS and organic content
- Biochemical oxygen demand
- Dissolved oxygen (DO)
- Hydraulic retention time (HRT)
- Food to microorganism (F/M) ratio

While, all of these parameters have been used to size facilities, the most commonly used are the DO and the HRT.

3. LITERATURE REVIEW

Water is an essential component to all known forms of life. About three-quarters of the earth surface is covered with water (about 1.4 billion km^3) occupying ~ 97% as seawater and ~ 3% as fresh water. Around two-third of the fresh water is in icebergs and glaciers. Availability of fresh water for our daily life activities, agriculture and industries, etc. is only 0.8% of the total amount of water present on earth.

Increasing urbanization, industrialization and changing life style has polluted the fresh water resources potentially termed as water pollution. Water pollution has become a universal problem now a day's affecting our sustenance on this planet. Government has set up laws regarding the conservation of this resource still over and misuse of water bodies draw the attention towards the evaluation of water resource policy to counter this problem. Worldwide increase in water pollution leads to deaths and diseases and studies estimated that approximately 14000 people die daily due to this problem only (West and Pink, 2006). The problem of water pollution is faced by both developed as well as developing countries. The industrial revolution has played a massive role in changing the socio-economic scenario of the modern world. Despite of a large numbers of merits of industrial revolution; it is the one of the major causes for the water pollution. All industries depend on fresh water resources and consume higher percentage of these resources for their growth.

The pulp and paper industry is one of the major production units that intensively use the fresh water resources for its production and ranks third in the world after the metals and the chemical industry on the basis of water consumption. Different steps involved in paper making started from raw material processing to furnished products utilize the high amount of water. The sustainable use of water resources becomes the most important environmental concerns in this industry. The manufacturing of paper releases considerable amount of wastewater about $60m^3$/ton of paper produced which affects the aquatic life and human health if discharged to the water-bodies without adequate treatment (Thompson et al., 2001). Bleaching is the crucial part of papermaking that utilizes the highest amount of water resources and also generates the highest wastewater loaded with toxic compounds than all other papermaking processes (Singh and Dutt, 2012).

Bleaching effluents are significantly loaded with high biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (mainly fibers), fatty acids, tannins, resin acids, lignin and its derivatives. The potential effect of toxicity depends on the type of raw materials and bleaching chemicals used for papermaking (Covinich et al., 2014). The characteristics of effluent generated in different processes of pulp and paper mill effluent is depicted in **Figure 1**.

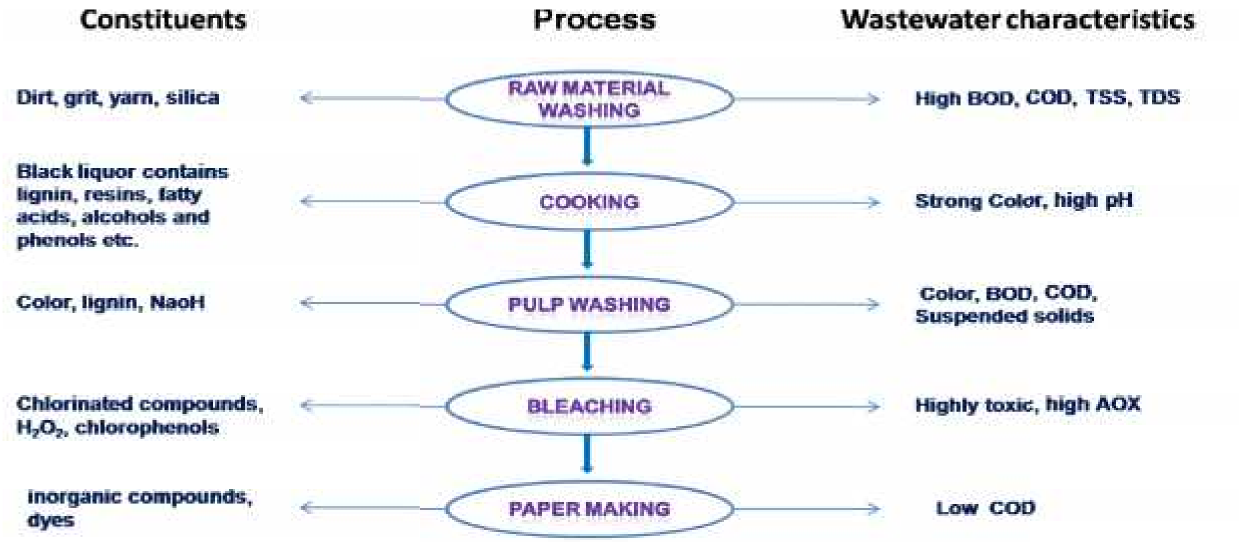

Figure 1: Characteristics and constituents of wastewater generated in various process of pulp and paper industry

Various oxidation-substitution reactions of bleaching chemicals such as the chlorine and its derivatives result in generation of chloro-lignin compounds (Kaur et al., 2017). Conventional bleaching based on chlorine and its derivatives discharge about more than 500 toxic chloro-lignin compounds in the bleaching effluents. Ministry of Environment and Forests, India, has categorized this industry in the Red Category list of 17 industries causing high pollution (Kumar et al., 2015).

Keeping in mind the hazardous effects of untreated and partially wastewater, it becomes mandatory to reduce the pollution load of paper mill effluents to protect the natural water bodies and health of the organisms as per discharge norms **(Table 1)**.

Wastewater treatment

Pollution abatement can be done by in plant modifications or end of the pipe treatment. Due to internal process change, the integrated and non-integrated pulp and paper mills generate about 60-125 m^3/tp and 10-50 m^3/tp of wastewater, respectively, which was earlier approximately 250 m^3/tp (Thapliyal and Tyagi, 2015). In plant, modification may be helpful to reduce the wastewater load but it is not possible to reduce the pollution of the effluents below prescribed limit without end of the pipe treatments. Different treatment processes till date utilized by industries to treat their effluent at end pipe are summarized below point to point.

Table 1: Discharge norms of different parameters of wastewater

Parameters	Description	Discharge Norms (As per recent norms)
pH	The influence of acid and alkaline of the water depends on the presence of hydrogen ions in water.	6.5 - 8.5
TDS, mg/L	The total dissolved solids in water are commonly used to denote the concentration of minerals dissolved.	2100
TSS, mg/L	The suspended solids are organic and inorganic compounds found in water.	30
Colour, Pt-Co unit	When impurities are mixed with water, water might appear in dark colour.	350
BOD, mg/L	The quantity of oxygen, utilized by micro organisms for biological degradation of the organic matter.	20
COD, mg/L	The quantity of oxygen needed to chemically oxidize the organic compound converted to CO_2 and H_2O.	200
AOX, mg/L	AOX is sum of organics including chlorine, bromine or iodine.	10
SAR (Sodium adsorption ratio)	SAR expresses ration shows the relative concentration of sodium to calcium and magnesium.	10

Physicochemical treatment

Physicochemical treatment processes include removal of suspended solids, colloidal particles, floating matters, colour, and toxic compounds by sedimentation, flotation, coagulation and flocculation.

Sedimentation and flotation

Sedimentation technology is the meekest and most economical method of separating solid substances from the liquid phase. The suspended matters present in the pulp and paper wastewater are comprised primarily of bark particles, fiber, fiber debris, filler and coating materials. These particles separated from liquid phase by gravity.

Coagulation and flocculation

Coagulation-flocculation is the most commonly applied process for treatment of wastewater. The mechanism of coagulation and flocculation are interconnected to each other for treating the wastewater such that coagulant neutralizes the electric charge on colloids presents in wastewater and keeps them in suspension and flocculant brings together these microscopic neutralized colloidal particles to form larger agglomerations through its binding action property which results in sedimentation of heavy particle at surface with time (Ebeling et al., 2003). The efficiency of the coagulation–flocculation process mainly depends on the subsequent factors such as type of coagulant and its dosage, pH of solution, temperature, ion strength, mixing time, agitation speed, concentration and nature of the organic compounds in the wastewater (Muralidhara, 1986; Randtke, 1988; Taylor et al., 2002).

In earlier 90s the commonly used coagulants during the coagulation/flocculation process were hydrolyzing metal salts of aluminum andiron such as $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$, and $Fe_2(SO_4)_3$ (Yang et al., 2010; Godosde et al., 2011). The major drawbacks of these metal coagulants are; when these are added to water they get hydrolyzed rapidly and forming a series of metal hydrolysis species. It results in high residual concentration of Al in the treated water that poses severe threats to human health and the environment (Zeng & Park, 2009). To overcome this problem, recently, high molecular weight long-chain polymers have been used as replacements for alum and ferric chloride such as PAC (Poly-aluminum chloride). These polymers provide many advantages in contrast to traditionally used flocs such as low dosage, easier storage and mixing, no pH adjustment is required, low capital cost and improved floc resistance to shear forces (Ebeling et al., 2003). This process is highly effective and economical but its major limitation is of it the generation of chemical sludge (Hai et al., 2007).

Advanced oxidation process

Due to the problems associated with conventional methods and in order to meet the stringent discharge limits set by pollution control boards, it becomes important to develop more technically advanced systems to reduce refractory organic compounds and color of wastewater (Kyoung and Son, 2011). Advanced oxidation processes (AOP) are the most promising technologies for the treatment of pulp and paper bleach effluents.

It oxidizes the complex organic recalcitrant compounds of wastewater that are hard to degrade into more biodegradable and harmless substances. The mechanism of AOPs are based on hydroxide radical which is the most reactive oxidizing agent in water treatment having strong oxidation potential between 2.8 V (pH 0) and 1.95 V (pH 14) (Tchobanoglous et al., 2003). Several technologies such as Fenton, photo-Fenton, ozonation etc. are included in this group and difference between them is source of radical production (Sandip et al., 2011).

These high energy hydroxyl radicals, attack most of organic molecules such as aromatic rings (benzene, toluene, ethylbenzene, xylene- BTXE), polyphenols, halogenated compounds (trichloroethane, trichlorethylene), resin acids, unsaturated fatty acids, volatile organic compounds (VOCs), pentachlorophenol (PCP), nitro phenols, detergents and pesticides, as well as inorganic contaminants such as cyanides, sulfides and nitrites (Munter, 2001).

The strength of the oxidative processes is that they do not transfer contaminants from one medium to another as happen in conventional techniques such as sedimentation, coagulation and flocculation etc. These processes also have negative aspects in terms of the high investment and operating costs (Moro et al., 2013).

Biological treatment

Biological treatment of wastewater is evaluated as good treatment processes for industrial effluents such as pulp and paper mills which is loaded with high amount of toxic organic compounds and degrade them into harmless inorganic solids either by aerobic or anaerobic process.

Aerobic treatment

In this treatment, oxygen is required by aerobic microorganisms to support their metabolic activity and is supplied in the form of air by aeration equipment. There are numerous types of aerobic systems available for degradation of toxic organic compounds in industrial wastewater and most common is activated sludge system (Persson, 2011). In ASP, wastewater is treated with a high concentration of microorganism such as bacteria, protozoa, fungi, and rotifers with powerful aeration and retention time of 8–12 hrs. This process works well as long as the consortium of microorganisms, usually termed as sludge grows in a healthy way and settles. The efficiency of this system depends upon the F/M ratio i.e. food to microbe ratio should be in equilibrium in the range of 0.2 to 0.5 (Virendra et al., 2014).

A high F/M ratio means that there is a large amount of food (such as BOD and COD) comparative to the number of microorganisms available to consume that food. Due to this microorganisms multiply rapidly and remain suspended in reactor which results in poor formation of floc and less degradation of organic matter. The F/M ratio is calculated by the formula given below

$$\frac{F}{M}=\frac{\left(BOD_5\frac{mg}{L}\right)\times\left(Flow\frac{MG}{day}\right)\times\left(8.34\frac{lb}{gal}\right)}{\left(MLVSS\frac{mg}{L}\right)\times\left(Aeration\ Volume,\ MG\right)\times\left(8.34\frac{lb}{gal}\right)}$$

Anaerobic treatment

The pulp and paper mills generate large amount of wastewater loaded with organic material which is converted to renewable energy in form of methane (CH_4) and carbon dioxide (CO_2). This process is carried out in absence of oxygen and applied to few selected streams such as raw material washing effluent of agro based pulp and paper mill have high COD color and BOD as compared to hardwood processing mills (Yang et al., 2010). The major limitation of anaerobic wastewater treatment includes the slow microbial substrate removal rate and slow biomass growth rate as compared to aerobic process (Rajagopal et al., 2013). Due to lower sludge production and chemical consumption; smaller space requirements and energy production in the form of bio gas make this technology more suitable for wastewater treatment than aerobic technology.

4. OBJECTIVES

(i) Characterization of wastewater from agro based pulp and paper mills for recalcitrant organic compounds (ROM) and other contaminants

(ii) Improvement in the biological treatment by augmentation of attached growth of organisms and/or dispersed nature of efficient organisms

(iii) Development of techno-economical process for removal of ROM with coagulants, flocculants and advanced oxidation process

5. SCOPE

- ✓ Collection of wastewater from sectional streams and wastewater treatment plant of agro base pulp and paper mills and characterization for total COD, soluble COD, BOD, charge, AOX and colour etc.
- ✓ Process development and application of efficient microorganisms in dispersed and/or attached growth process for treatment of wastewater from agro based pulp and paper mills
- ✓ Evaluation of performance of conventional activated sludge processwith combined packed reactor (attached growth) followed by activated sludge process, augmented with efficient organisms, for treatment of wastewater
- ✓ Identification and selection of cost effective coagulants and flocculants for treatment of biologically treated wastewater for removal of ROM
- ✓ Characterization of chemical sludge and identification of techno-economical solution for handling and disposal of chemical sludge
- ✓ Validation of findings by CPPRI
- ✓ Demonstration of process at mill site

6. MATERIALS AND METHODS

6.1. Materials

6.1.1. Wastewater

The wastewater, used in this project, was collected from one of the agro based pulp and paper mill in North India.

6.1.2.Treatment chemicals for wastewater

a) Alum and PAC were used as Coagulants and anionic flocculant used for flocculation.
b) Ozone and H_2O_2 were used as advance oxidative chemicals for degradation of organic materials present in wastewater.
c) Different lignin degradation chemicals such as lignoclean-8, 11, 18 and 22 having various solids content 16%, 24%, 34% and 42%, respectively were used to degrade lignin present in wastewater.
d) The enzyme used with activated sludge process to treat the wastewater of agro-based pulp and paper mill **(Table 2)**.

Table 2: Description of chemicals/enzyme used under study

S. No.	Chemicals	Description of chemicals	Cost, Rs./kg (as such)
1	Alum	Aluminium sulphate	7.0
2	PAC	Poly-aluminium chloride	3.0
3	Anionic flocculant	AF-5540	250.0
4	Ozone	O_3	100.0
5	H_2O_2	Hydrogen peroxide	70.0
6	Lignin degrade	Lignoclean-8	3.0
7	Lignin degrade	Lignoclean-11	5.0
8	Lignin degrade	Lignoclean-18	20.0
9	Lignin degrade	Lignoclean-22	40.0
10	Enzyme	Laccase	-

6.1.3.Collection of wastewater

a) Different streams of mill such as mill effluent, wet washing before and after anaerobic treatment, mixed feed and final discharge were collected.
b) The wastewater of different streams, collected from agro based mill, was stored at 4ºC.

6.1.4. Standard methods for wastewater

The wastewater was analyzed for various parameters using standard methods **(Table 3)**.

Table 3: Various wastewater parameters and their standard method

Parameters	**Standard method**
pH	IS: 3025 (Part 11)-1983, 1st revision, Reaffirmed 2006, Electrometric Method
COD	IS: 3025 (Part 58)-2006, 1st revision, 2006.
BOD	IS: 3025 (Part 44)-1993, 1st revision,1st amendment, Reaffirmed, 2009
Colour	APHA 23nd edition 2017, 2120 C
TSS	IS: 3025 (Part 17)-1984,1st revision, 1st amendment, Reaffirmed 2012
TDS	IS: 3025 (Part 16)-1984,1st revision,1st amendment, Reprint 2008
SAR	APHA 23nd edition 2017, 3111 B
AOX	ISO: 9562; 2004

a) The samples of colour were prepared by using method APHA 23rd edition 2017, 2120 C and analyzed the values by using UV/Visible spectrophotometer (Varians). The AOX measurements were done by using AOX analyzer (Thermo scientific). All the analysis was carried out in duplicates.

b) For mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS), 100 ml of mixed sludge sample was centrifuged and washed with distilled water before transferring to pre-weighed silica crucible. The sample was oven dried at 105°C over night. Dried material was taken as MLSS and the same crucible was ignited at550ºC and loss in weight was taken as MLVSS.

c) DO was determined using YSI make DO meter and morphological characterization of organisms was done with image analyzer make Zeiss.

6.1.5. Preparation of Chemicals

a) **Alum:**The concentration of 10,000 mg/L of alum prepared by weighing 2.5 g of alum and dissolved in 250 ml volume of Grade-1 laboratory water.

b) **Flocculant:** The concentration of 1,000 mg/L of AF-5540 prepared by weighing 0.1 g of AF-5540 dissolved in 100 ml volume of Grade-1 laboratory water.

c) **PAC:** The PAC with solid content 18% and density 1.25 g/mL was used as such for treatment.

d) **Ozone:** The gaseous ozone was generated from oxygen by ozone generator. The given ozone concentration in the gas stream was measured using the potassium iodide method (IOA Standardization committee 001/87) in order to calculate the applied ozone dose and residual ozone dose.

6.1.6. Activated sludge process

Activated sludge samples from the agro-based pulp and paper mill along with cow dung were used for the seeding in the biological reactors. Before seeding in bioreactors, organisms were acclimatized under controlled environment in batch reactor for 2 weeks by maintaining the following parameters **(Table 4)**.

Table 4: Stabilization of various reactor's parameters

Parameters	Values
MLSS, g/L	4.0±1.1
MLVSS, g/L	3.0±0.7
Organic content, %	75±3.2
DO, mg/L	1.0±0.2
HRT, hrs	10±0.3

6.1.7.Calculation of reactor parameters

$$(\text{MLSS}), g/L = \frac{\text{W2} - \text{W1 (g)}}{\text{Sample volume (mL)}} \text{ x } 1000$$

$$(\text{MLVSS}), g/L = \frac{\text{W2} - \text{W3 (g)}}{\text{Sample volume (mL)}} \text{ x } 1000$$

Where, W1 = OD wt. of crucible; W2 =OD wt. of crucible and OD sludge; W3 = OD wt. of crucible and Ash

$$\text{Organic Content in sludge, \%} = \frac{\text{MLSS (g/L)}}{\text{MLVSS (g/L)}} \text{ x 100}$$

$$\text{HRT, hrs} = \frac{\text{Reactor Volume (L)}}{\text{Volume of wastewater treated(L) / Time(hrs)}}$$

$$\text{Percent Removal, \%} = \frac{\text{Influen: − Wastewater}}{\text{Influen}} \text{ x 100}$$

CHAPTER – 1

Post-treatment of ASP outlet with H_2O_2

7.1. Characterization of wastewater

Characterization of different streams collected from agro-based pulp and paper mill were done **(Table 5)**. The mill wastewater, wet washing before and after anaerobic treatment wastewaters were slightly basic in nature and having COD 1388±94, 4949±178 and 1667±81 mg/L, respectively. The colour of mill wastewater, wet washing before and after anaerobic treatment wastewaters were 950±24, 10448±221and 3896±155 Pt-Co unit, respectively. The mixed wastewater was also slightly basic in nature and its COD and colour were 1575±62mg/L and 2867±109 Pt-Co unit, respectively. The mill wastewater and wet washing after anaerobic treatment were mixed in ratio of 7:3 before being sent to ASP.

Table 5: Characterization of wastewater collected

Parameter	Units	Mill wastewater	Wet washing before anaerobic treatment	Wet washing after anaerobic treatment	Mixed wastewater
pH	-	7.15±0.12	6.96±0.16	7.43±0.22	7.55±0.15
COD	mg/L	1388±94	4949±178	1667±81	1575±62
Colour	Pt-Co unit	950±24	10448±221	3896±155	2867±109

7.2. Optimization of H_2O_2 dose

7.2.1. Optimization of mixing time for H_2O_2 with ASP treated wastewater

The wastewater seeded with initial COD 1575±62 mg/L and colour 2867±109 Pt-Co unit in ASP. The feed treated in ASP reactor with temp. 37.0°C and DO 1.0 mg/L. The MLSS, MLVSS and Organic content was maintained 3.84±0.40, 2.59±0.34 and 67.45±4.18 in the reactor. The HRT was 10.0±0.21 hrs. The ASP reduced the COD 54.9±2.1% (710±15 mg/L) and colour up to 22.0±1.5% (2232 Pt-Co unit). The H_2O_2 was added in ASP treated wastewater at fixed dose 0.01% and for different mixing time (min.). At minimum mixing time 50 minutes with fixed dose of 0.01% of H_2O_2 the COD reduction was 54.9±2.1% and colour reduction was 22.0±0.4%. The maximum COD reduction of56.9±1.5% and colour reduction of 42.6±1.0% was found at100 min. mixing time. The results were shown in **Table 6, Figure 2**.

Table 6: Optimization of different mixing time for H_2O_2 dose (0.01%) with ASP treated wastewater

Sample	Mixing time, min.	pH	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %
Feed	-	7.55	1575	-	2862	-
Control	0	7.69	824	47.7	2232	22.0
Treated with 0.01% H_2O_2	50	7.11	711	54.9	2092	26.9
	60	7.25	709	55.0	2001	30.1
	70	7.26	706	55.2	1895	33.8
	80	7.51	699	55.6	1875	34.5
	90	7.63	701	55.5	1766	38.3
	100	7.65	682	56.7	1666	41.8
	110	7.55	679	56.9	1643	42.6

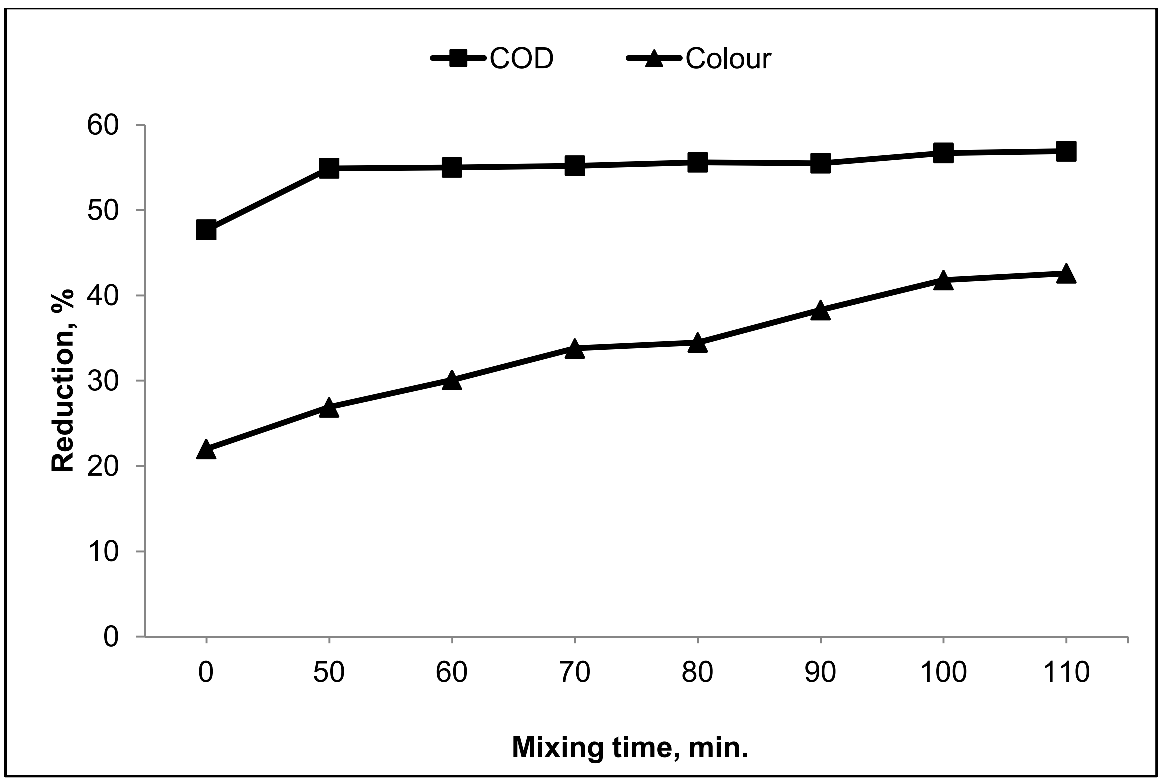

Figure 2: Graphical representation of effect of different mixing time of H_2O_2 on COD and colour reduction

CHAPTER – 2

Post-treatment of ASP outlet with ozone

8. Ozone treatment

8.1. Two stage lab scale reactors as activated sludge process (ASP 1 and ASP 2) for wastewater treatment

The laboratory scale activated sludge process bioreactors were run for 2 months on the prepared feed (Mill wastewater and wet washing after anaerobic in the ratio of 7:3) to establish the baseline performance.

8.2. COD and colour reductions of feed in ASP1 treatment

The MLSS and MLVSS maintained of the ASP 1 were maintained 3.16±1.04 g/L and 2.19±0.73 g/L, respectively with organic content of 69.3±3.66% **(Table 7)**. The wastewater was fed as feed with initial COD and colour 1575±62 mg/L and 2867±109 Pt-Co unit, respectively to the ASP 1 (ASP 1) to obtain the stable results up to its maximum capacity to reduce the COD and colour. The ASP 1 reduced the COD 47.5% and colour up to 22.8% **(Table 8)**.

8.3. Impact of O_3 doses on ASP1 treated wastewater

The MLSS and MLVSS of the ASP 2 were maintained at 2.85±0.82 g/L and 1.99±0.57 g/L, respectively with organic content of 69.1±2.90% **(Table 7)**. The wastewater treated with ASP 1 was fed as feed to ASP 2 with initial COD and colour 827±48 mg/L and 2210±102 Pt-Co unit, respectively to further reduce COD and colour. The ASP 2 reduced the COD 60.7±1.5% and colour up to 55.3±1.0%.

Table 7: MLSS, MLVSS, organic content and HRT maintained in the reactor ASP 1 and ASP 2

ASP	MLSS, g/L	MLVSS, g/L	Organic content, %	HRT, hrs
ASP 1	3.16±1.04	2.19±0.73	69.3±3.66	10.0±0.31
ASP 2	2.85±0.82	1.99±0.57	69.1±2.90	10.0±0.12

Table 8: COD and colour reductions of Feed in ASP1 treatment

Sample	pH	COD, mg/L	Reduction (w.r.t. initial feed), %	Colour, Pt-Co unit	Reduction (w.r.t. initial feed), %
Feed	7.55	1575	-	2862	-
After ASP1	7.85	827	47.5	2210	22.8

8.4. Ozone treatment

The ASP 2 treated wastewater sample, having COD 325 mg/L and colour 987 Pt-Co unit, was treated with ozone at two doses**.** The ozone treatment was given in the 2 L closed vessel. ASP 2 treated wastewater was taken in closed vessel and allowed to pass the ozone through wastewater with proper mixing. The COD and colour parameters at the 49 mg/L dose were 303 mg/L and 254±23 Pt-Co unit. At the dose of 49 mg/L, the maximum reduction of COD and colour was 80.8 and 91.1% (w.r.t. initial feed), respectively **(Table 9, Figure 3)**. The colour was under discharge norms but COD exceeded the discharge norms. The ozone treatment is found to be ineffective towards COD reduction, but effective for colour reduction.

Table 9: Impact of two different doses of O_3 dose on AT1 (ASP) treated wastewater

Sample	Ozone dose, mg/L	pH	COD, mg/L	Reduction (w.r.t. ASP 2), %	Reduction (w.r.t. initial feed), %	Colour, Pt-Co unit	Reduction (w.r.t. ASP 2), %	Reduction (w.r.t. initial feed), %
After ASP2	-	7.86	325	60.7	79.4	987	55.3	65.5
After ASP2 (Treated with O_3)	27	7.69	312	62.3	80.2	341	84.6	88.1
	49	7.63	303	63.4	80.8	254	88.5	91.1

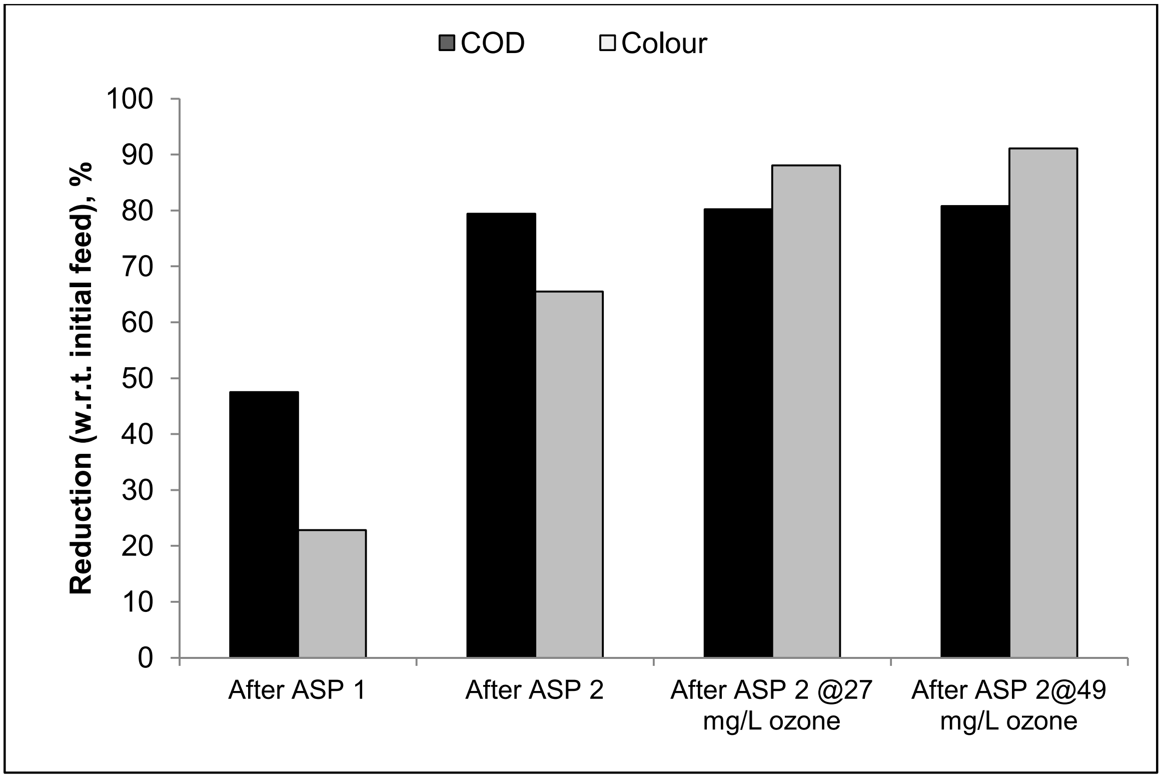

Figure 3: Graphical representation of COD and colour reduction (%) with respect to initial feed at various doses of ozone

CHAPTER – 3

Pre and post-ASP treatment with alum

9. Pre-treatment of WWAA with alum

9.1.Optimization of alum dose with fixed dose of AF-5540 for pre-treatment of WWAA

The WWAA having initial COD 1667±81 mg/L and colour 3896±155 Pt-Co unit was treated with alum ranging from 1.25 to 6.25 ton/day (i.e. 0.05 to 0.25% based on 2500 m^3/day WWAA generation). The minimum dose 1.25 ton/day with anionic flocculant (dose 10 kg/day) showed the COD, colour reduction up to 16.7±0.7% and 22.4±0.6% respectively. The optimized dose 3.75 ton/day for pre-treatment revealed the COD and colour reduction of 45.1±1.4% and 74.3±2.6%, respectively **(Table 10, Figure 4)**. The COD and colour values at optimized dose were 916±56 mg/L and 1003±49 Pt-Co unit, respectively.

Table 10: Effect of alum doses (with fixed dose of AF-5540) for pre-treatment of WWAA

Alum, ton/day (%)	AF-5540, kg/day	pH	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %	Treatment cost, Rs./m^3
-	-	8.65	1667		3896		
1.25 (0.05)	10	8.39	1389	16.7	3025	22.4	4.5
2.50 (0.10)		8.16	1250	25.0	2311	40.7	8.0
3.75 (0.15)		8.14	916	45.1	1003	74.3	11.5
5.00 (0.20)		8.06	722	56.7	489	87.4	15.0
6.25 (0.25)		7.68	694	58.4	281	92.8	18.5

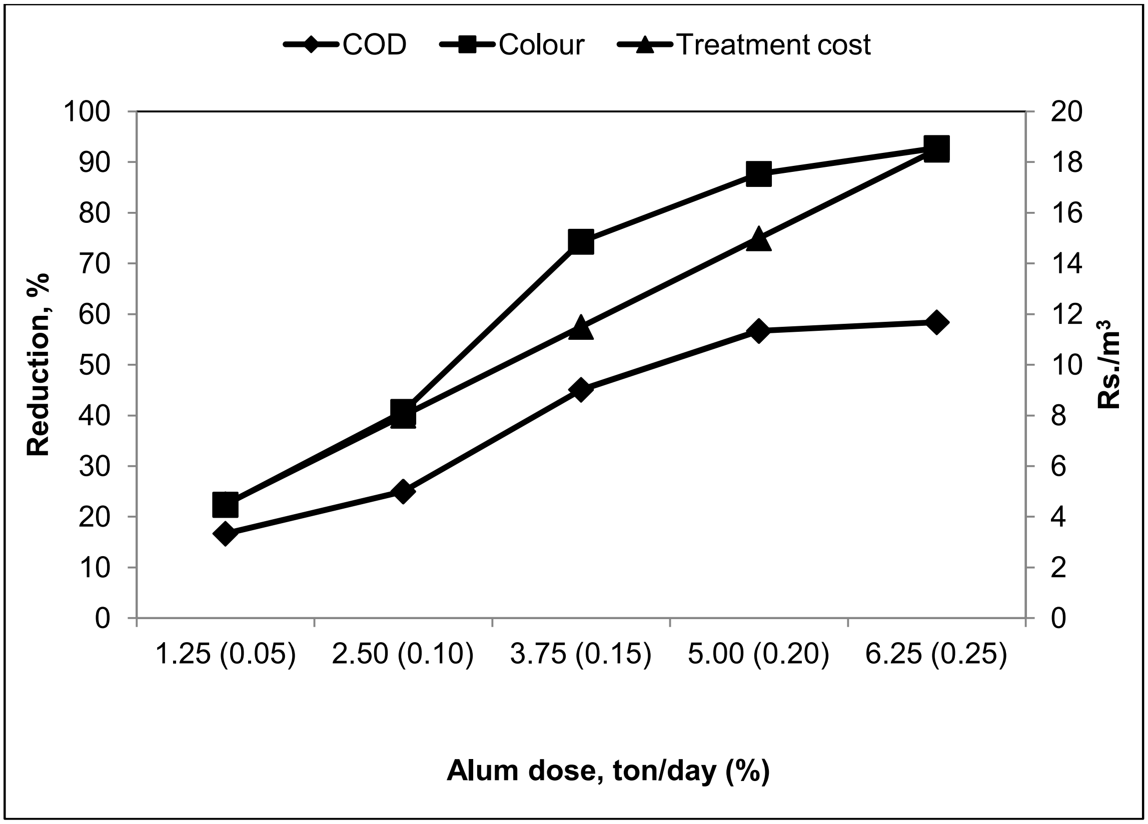

Figure 4: Graphical representation of effect of alum doses (with fixed dose of AF-5540 10 kg/day) for pre-treatment of WWAA

9.2. Comparison of feed as such (F1) with pre-treated Feed (F2) with alum and AF-5540

The mill wastewater and WWAA was mixed in ratio of 7:3 consider as 'control feed' (F1). The feed was slightly basic in nature having COD 1575±62mg/L and colour 2867±109 Pt-Co unit.

Feed, F2: The pre-treatment of WWAA was done at alum dose 3.75 ton/day and kept for 2 hrs for settling of sludge. The mill wastewater and supernatant of WWAA mixed in the ratio of 7:3 respectively. The pH of feed was 6.94, the COD and colour was 1246±56 mg/L and 841±36 Pt-Co unit, respectively. This feed is considered as 'alum treated feed' COD and color of 'control feed' and 'alum treated feed' **(Table 11)**.

Table 11: Comparison between pH, COD and colour parameters of control feed and alum treated feed.

Feed	Pre- treatment (alum), ton/day (%)	AF-5540, kg/day (ppm)	pH	COD, mg/L	Colour, Pt-Co unit
Feed F1 (control)	-	-	8.16	1575	2862
Feed F2 (pre-treated with alum)	3.75 (0.15)	10 (4)	7.94	1246	841

9.3. Effect of pre-treatment (using alum+AF-5540) on ASP performance

The Control feed treated in ASP reactor R-I with temp. 37.0±1°C, DO 1.0±0.2 mg/L was considered as Control. The same conditions maintained in another reactor R-II seeded with Alum treated feed against R-I (control).The MLSS, MLVSS and organic content were maintained 3.26±0.94, 2.39±0.83 and 73.3±2.26 respectively, in control reactor (R-I) **(Table 12)**. The HRT was 10.1±0.21 in R-I. The COD reduction was 47.7±0.9% and colour reduction was 22.0±0.5% in control reactor R-I. The COD reduction and colour reduction was achieved 52.9±0.7% and 51.0±0.8% in R-II **(Table 13)**. The feeding COD and colour plays a crucial role in biological system reduction. The reduction efficiency is supposed to increase with the reduction in initial loading of COD and colour.

Table 12: Reactor parameters including MLSS, MLVSS, organic content and HRT

Reactors	MLSS, g/L	MLVSS, g/L	Organic content, %	HRT, hrs
R-I (ASPF1)	3.26±0.94	2.39±0.73	73.3±2.26	10.0±0.21
R-II (ASPF2)	3.41±1.04	2.33±0.78	68.3±3.67	10.0±0.42

Table 13: Effect of pre-treatment of WWAA (using alum) on ASP performance

Samples	pH	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %
Feed F1 (control)	8.16	1575	-	2867	-
***ASP_{F1}(control)**	8.23	824	47.7	2232	22.1
Feed F2 (pre-treated with alum)	7.94	1246	-	841	-
***ASP_{F2}**	8.30	586	53.0	412	51.0

*****ASP_{F1} andASP_{F2} are the ASP treated wastewaters fed with F1 and F2, respectively**.**

9.4. Post-treatment of ASP outlet (with alum+AF-5540) fed with feed F1

9.4.1. Impact of alum doses

The wastewater samples were collected after ASP from the reactor R-I for further treatment. The pH, COD and colour of sample collected from control reactor were 8.23±0.2, 824±24 mg/L and 2232±102 Pt-Co unit, respectively. The different alum doses (4.35 to 8.70 ton/day) with fixed dose (35 kg/day) of AF-5540 were used for treatment of ASP outlet. At minimum dose of 4.35 ton/day of alum the COD reduction was 66.5% and colour reduction was 72.5%. The optimum dose was 8.70 ton/day at which COD reduction was 88.1% and colour reduction was 91.6%. There is no need of increasing the dose beyond 8.70 ton/day the values of COD and colour were within discharge norms. Therefore we concluded that the alum dose of 8.7 ton/day was fit for the post-treatment after ASP wastewater **(Table 14, Figure 5)**.

Table 14: Impact of different alum doses in post-treatment of ASP outlet fed with feed F1

Samples	Alum, ton/day, (%)	AF-5540, kg/day (ppm)	pH	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %
Feed, F1 (inlet to ASP)	-	-	8.16	1575	-	2867	-
ASP_{F1}	-	-	8.23	824	47.6	2232	22.1
Doses of alum for post-treatment	4.35 (0.05)	34.8 (4)	7.95	527	66.5	787	72.5
	5.22 (0.06)		7.91	512	67.5	440	84.7
	6.09 (0.07)		7.43	450	71.4	321	88.8
	6.96 (0.08)		7.41	387	75.4	301	89.5
	7.40 (0.085)		7.32	300	80.9	298	89.6
	7.83 (0.09)		7.25	245	84.4	268	90.7
	8.70 (0.10)		6.91	187	88.1	240	91.6

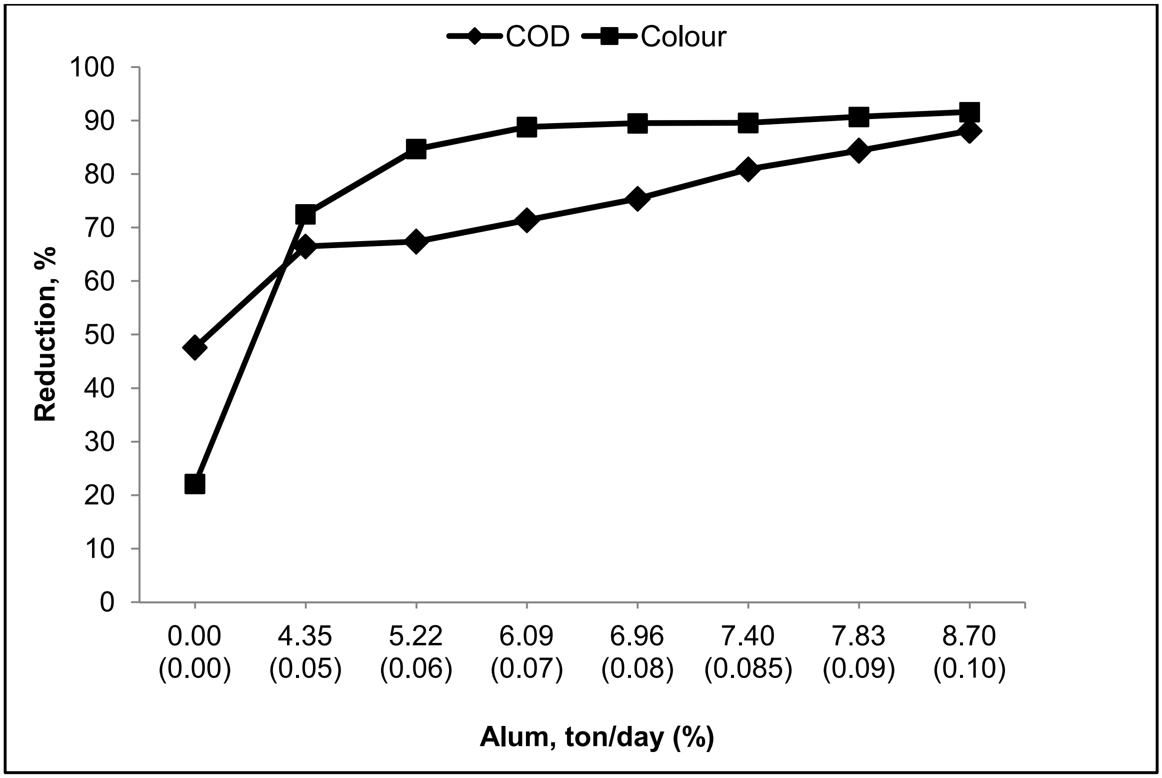

Figure 5: Graphical representation of impact of different alum doses (with fixed dose of AF-5540 34.8 kg/day) in post-treatment of ASP outlet fed with feed F1

9.5. Biological treatment (ASP) of feed F2 followed by post-treatment (alum+AF-5540)

9.5.1.Impact of different doses of alum on Post-treatment

The alum treated feed with initial pH 8.16 having COD 1246 mg/L and colour 841 Pt-Co unit treated with ASP in reactor R-II. The MLSS, MLVSS and Organic content was 3.41±1.04 mg/L, 2.33±0.78 mg/L and 68.33±3.67% for reactor R-II. The HRT was 10.0±0.42hrs in R-II shown in **Table 12**. The ASP showed the 53.0% reduction in COD and 51.0% in colour. The different alum doses with fixed dose of AF-5540 (34.8 kg/day based on 2500 m^3/day wet washing wastewater) introduced after ASP treatment. The minimum dose of 0.87 ton/day showed the pH 7.96 with final COD 486 mg/L and colour 354 Pt-Co unit. The optimum dose with 3.48 ton/day resulted in the final pH 7.43 with final COD 198 mg/L and colour 149 Pt-Co unit **(Table 15, Figure 6)**. At optimized doses, total Alum consumption was7.23 ton/day (3.75 ton/day pre-alum dose+3.48 ton/day post-alum dose) along with 44.8 kg/day AF-5540 (10 kg/day+34.8 kg/day) **(Table 16)**.

Table 15: Impact of different alum doses in post-treatment of ASP outlet fed with feed F2

Samples	Alum, ton/day (%)	AF-5540, kg/day (ppm)	pH	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %
Feed, F2 (inlet to ASP)	-	-	8.16	1246	-	841	-
ASP_{F2} (control)	0	0	8.23	586	53.0	412	51.0
Addition of different alum doses in post-treatment of ASP outlet fed with feed F2							
Alum doses	0.87 (0.01)	34.8 (4)	7.96	486	61.0	354	57.9
	1.74 (0.02)		7.95	405	67.5	302	64.1
	2.61 (0.03)		7.91	298	76.1	250	70.3
	3.48 (0.04)		7.43	198	84.1	212	74.8

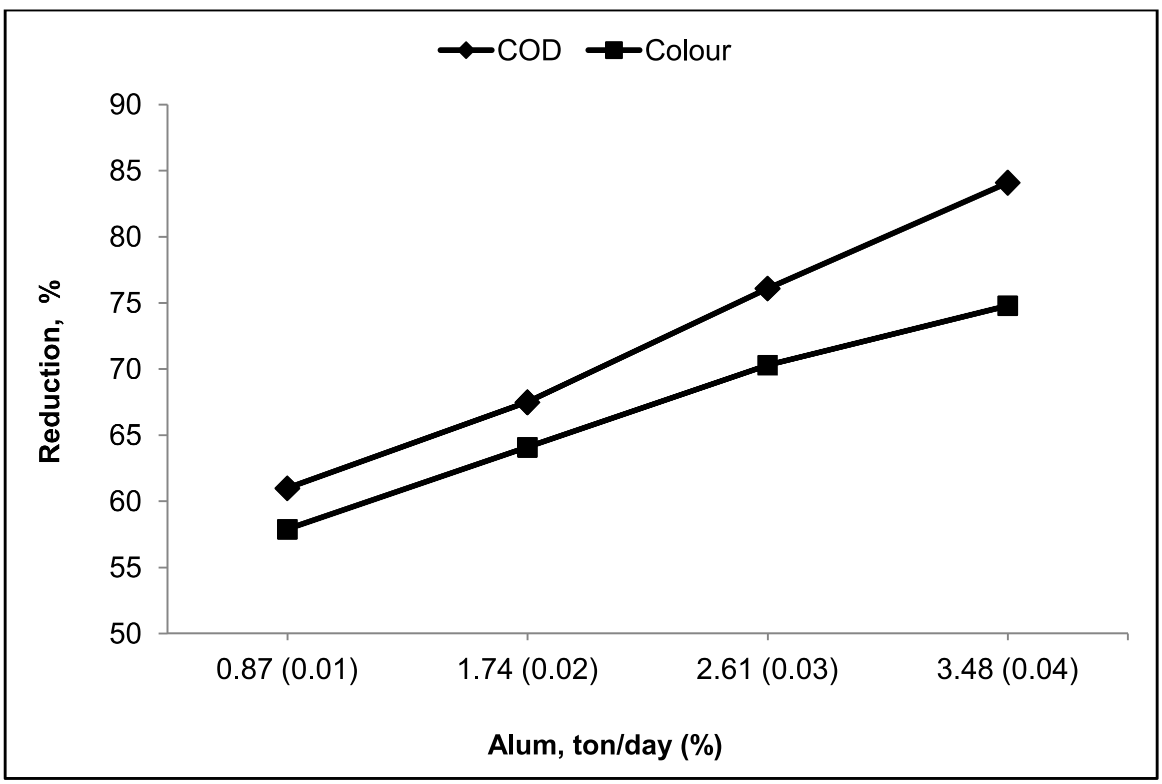

Figure 6: Graphical representation of impact of different alum doses (with fixed dose of AF-5540 34.8 kg/day) in post-treatment of ASP outlet fed with feed F2

Table 16: Summary of results for alum treatment

Approach	Pre-treatment		Post-treatment		Total consumption		Final discharge	
	Alum, ton/day (%)	AF-5540, kg/day (ppm)	Alum, ton/day (%)	AF-5540, kg/day (ppm)	Alum, ton/day	AF-5540, kg/day (ppm)	COD, mg/L	Colour, Pt-Co unit
Post-treatment of ASP outlet only	-	-	8.7 (0.1)	34.8 (4)	8.7	34.8 (4)	187	240
Pre-treatment of WWAA followed by post-treatment of ASP outlet	3.75 (0.15)	10 (4)	3.48 (0.04)	34.8 (4)	7.23	44.8 (5)	198	212

CHAPTER – 4

Effect of Lignoclean on lignin degradation of wastewater

10. Characteristics of wastewater

The initial pH, COD, colour and Lignin of ASP treated wastewater were 7.9±0.2, 524±21 mg/L, 1589±83 Pt-Co unit and 211±16 mg/L, respectively **(Table 17)**. The wastewater was treated with coagulant Lignoclean having different solid levels **(Table 18)**. The chemicals were cationic in nature. Lignoclean-8 and Lignoclean-11 were not found to be effective to degrade lignin significantly (data not shown here).

Table 17: Characterization of ASP treated wastewater collected

Parameter	Units	ASP treated wastewater
pH	_	7.98±0.2
COD	mg/L	524±21
colour	Pt-Co unit	1589±83
Lignin	mg/L	211±16

Table 18: Characterization of Lignoclean

S. No.	Lignoclean	Solid content, %
1	Lignoclean-8	16
2	Lignoclean-11	24
3	Lignoclean-18	34
4	Lignoclean-22	42

10.1. Optimization of Lignoclean-18 dose for lignin reduction

The different doses of lignoclean-18 used for ASP treated wastewater was ranging from 2.61 m^3/day to 6.09 m^3/day in combination with anionic flocculant AF-5540 at fixed dose of 8.7 kg/day (1 ppm). The flocculant was used to enhance the impact of coagulant on sample by forming the settling flocs. The minimum dose 2.61 m^3/day showed the reduction in lignin, colour and COD up to 44.0%, 61.4% and 9.7% respectively. The maximum dose 6.09 m^3/day showed the lignin, colour and COD reduction up to 76.3% (50 mg/L), 90.7% (147 Pt-Co unit) and 64.3% (187 mg/L) respectively **(Table 19, Figure 7)**.

Table 19: Optimization of dosesof Lignoclean-18 for lignin, colour and COD reduction

Sample	Lignoclean -18, m^3/day (%)	AF-5540, kg/day (ppm)	pH	Lignin, mg/L	Red., %	Colour Pt-Co unit	Red., %	COD, mg/L	Red., %
ASP treated wastewater	-	-	7.98	211	-	1589	-	524	-
	2.61 (0.03)	8.7 (1.0)	7.40	117	44.5	614	61.4	473	9.7
	3.48 (0.04)		7.20	91	56.9	401	74.8	372	29.0
	4.35 (0.05)		7.01	71	66.4	266	83.3	321	38.7
	5.22 (0.06)		6.89	59	72.0	193	87.9	235	55.2
	6.09 (0.07)		6.62	50	76.3	147	90.7	187	64.3

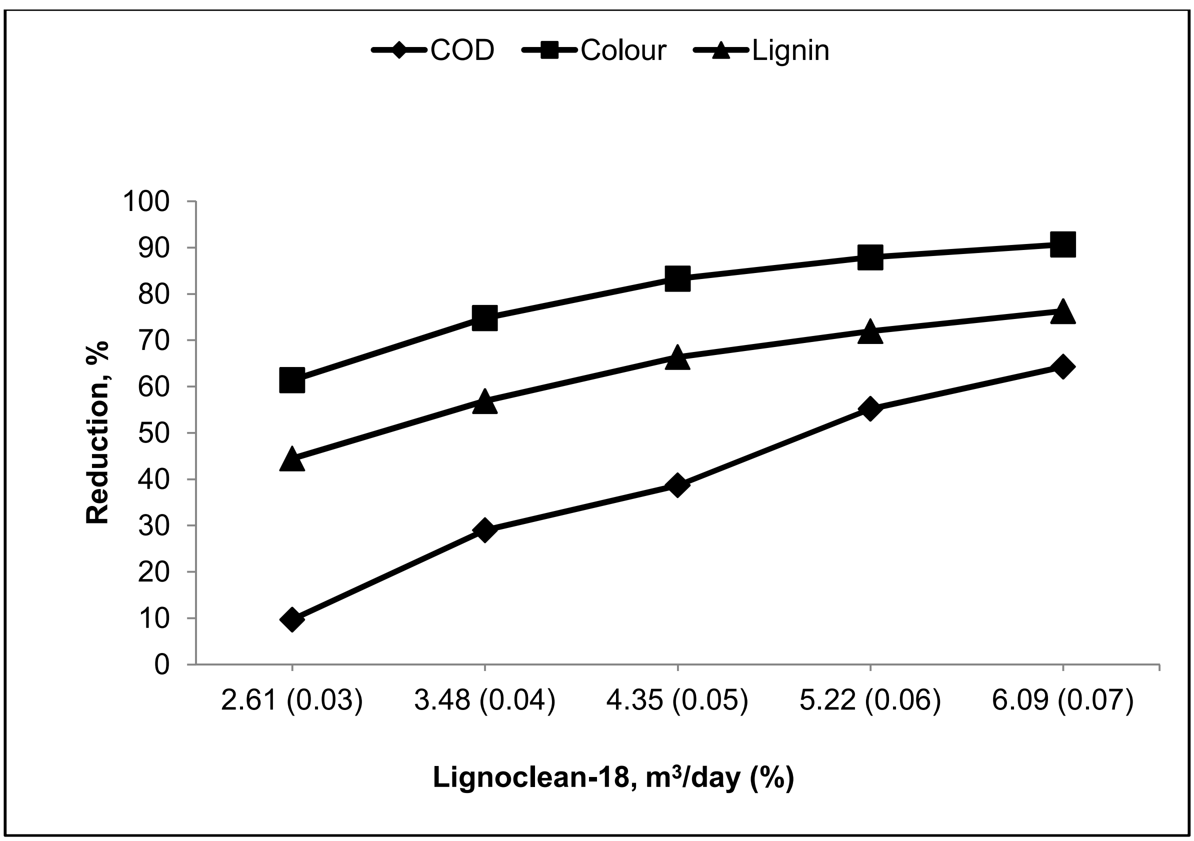

Figure 7: Graphical representation of effect of doses of Lignoclean-18 (with fixed dose of AF-5540 34.8 kg/day) for lignin, colour and COD reduction

10.2. Optimization of AF-5540 dose in combination with Lignoclean-18

The different doses of AF-5540 from 6.1 kg/day (0.7 ppm) to 17.4 kg/day (2 ppm)were used for lignin reduction in ASP treated wastewater in combination with fixed dose of Lignoclean-18 i.e. 6.09 m^3/day or 0.07%. The AF-5540 with minimum dose showed the lignin, colour and COD reduction up to 71.6%, 81.2% and 50.8% respectively. The optimized dose 8.7 kg/ day showed maximum reduction of lignin, colour and COD up to 76.8% (49 mg/L), 90.7% (147 Pt-Co unit) and 64.3% (187 mg/L) respectively, **(Table 20, Figure 8)**. The maximum dose 17.4 kg/day showed lignin, colour and COD reduction up to 70.6%, 81.9% and 51.5% respectively.

10.3. Optimization of Lignoclean-22 dose for lignin reduction

The different doses of lignoclean-22 used for ASP treated wastewater was ranging from 1.74 m^3/day to 3.48 m^3/day in combination with anionic flocculant AF-5540 at various doses (4.4 to 26.1 kg/day (0.5 to 3 ppm). The maximum reduction was obtained at 3.48 m^3/day Lignoclean-22 and 8.7 kg/ day AF-5540 by showing the lignin, colour and COD reduction up to 49.0% (98 mg/L), 73.5% (484 Pt-Co unit) and 40.4% (303mg/L) respectively. **(Table 21, Figure 9)**. Still, COD and colour parameters of the selected dose combination were not as per discharge norms.

Table 20: Optimization of AF-5540 dose with fixed Lignoclean-18 dose for lignin reduction

Sample	Lignoclean -18, m^3/day (%)	AF-5540, kg/day (ppm)	pH	Lignin, mg/L	Red., %	Colour, Pt-Co unit	Red., %	COD, mg/L	Red., %
ASP treated wastewater ASP treated wastewater	-	-	7.98	211	-	1589	-	524	-
	6.09 (0.07)	6.1 (0.7)	6.81	60	71.6	298	81.2	258	50.8
		8.7 (1.0)	6.62	49	76.8	147	90.7	187	64.3
		13.1 (1.5)	6.51	58	72.5	245	84.6	250	52.3
		17.4 (2.0)	6.35	62	70.6	287	81.9	254	51.5

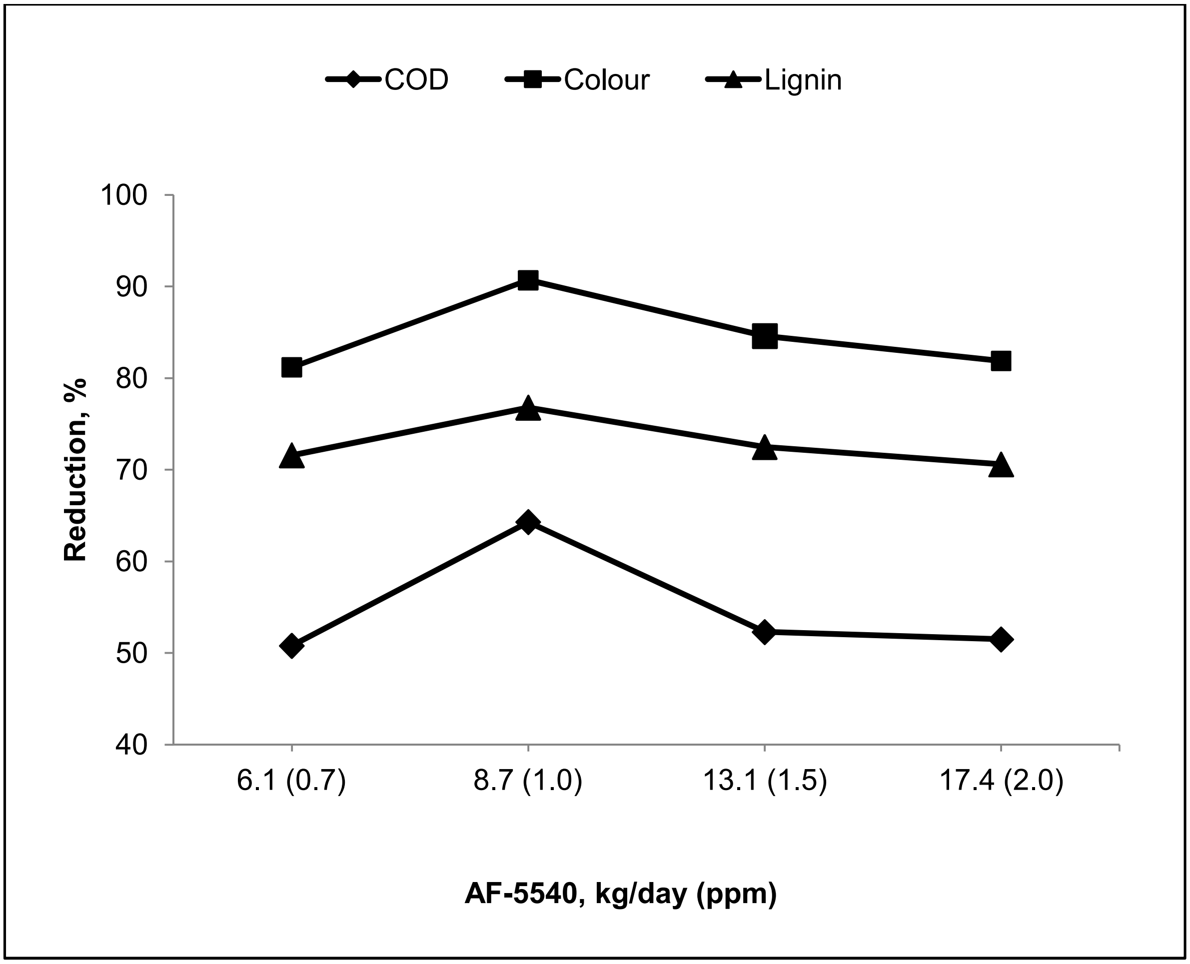

Figure 8: Effect of AF-5540 dose with fixed Lignoclean-18dose (6.09 m^3/day**)** for lignin reduction

Table 21: Optimization of doses of Lignoclean-22 and AF-5540 for lignin, colour and COD reduction

Sample	Lignoclean-22 , m^3/day (%)		AF-5540, kg/day(%)	pH	Lignin, mg/L	Red., %	Colour, Pt-Co unit	Red., %	COD, mg/L	Red., %
ASP treated waste-water	-		-	7.98	192	-	1826	-	508	-
	D1	1.74 (0.02)	4.4 (0.5)	7.73	130	32.3	805	55.9	418	17.7
	D2	2.61 (0.03)		7.56	115	40.1	644	64.7	352	30.7
	D3	3.48 (0.04)		7.52	107	44.3	567	68.9	344	32.3
	D4	1.74 (0.02)	8.7 (1.0)	7.42	121	37.0	718	60.7	377	25.8
	D5	2.61 (0.03)		7.41	120	37.5	719	60.6	373	26.6
	D6	3.48 (0.04)		7.33	98	49.0	484	73.5	303	40.4
	D7	1.74 (0.02)	17.4 (2.0)	7.51	132	31.3	852	53.3	434	14.6
	D8	2.61 (0.03)		7.39	116	39.6	662	63.7	402	20.9
	D9	3.48 (0.04)		7.39	103	46.4	534	70.8	361	28.9
	D10	1.74 (0.02)	26.1 (3.0)	7.55	131	31.8	819	55.1	393	22.6
	D11	2.61 (0.03)		7.46	111	42.2	610	66.6	336	33.9
	D12	3.48 (0.04)		7.37	106	44.8	572	68.7	311	38.8

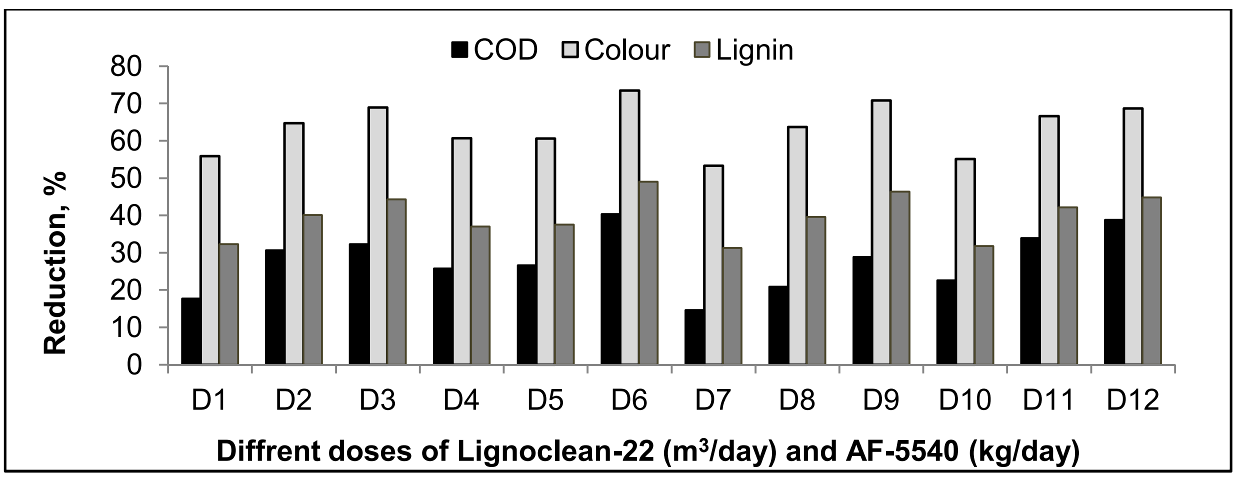

Figure 9: Graphical representation of effect of doses of Lignoclean-22 and AF-5540 for lignin, colour and COD reduction

CHAPTER – 5

Pre and Post-ASP treatment with PAC

11. Characteristics of wastewater collected for PAC treatment

The wastewater collected from agro-based pulp and paper mill was initially characterized. Various physico-chemical characteristics of different individual streams of wastewater are given in **Table 22**. The mill wastewater and wet washing after anaerobic treatment wastewaters were slightly basic in nature and having about 1379±49 and 1986±79 mg/L of COD, respectively. The colour and Pt-Co unit of mill wastewater and wet washing after anaerobic treatment wastewaters were 929±29 and 7640±259 respectively. The mixed wastewater was also slightly basic in nature and it COD, mg/L and colour, Pt-Co unit were 1734±66 and 3888±155 respectively. The mill wastewater and wet washing after anaerobic treatment were mixed in ratio of 7:3 before sent to ASP (activated sludge process).

Table 22: Characterization of wastewater collected

Parameter	pH	COD, mg/L	Colour, Pt-Co unit
Mill wastewater	7.15±0.14	1379±49	929±29
WWAA	7.43±0.62	1986±79	7640±259
Mixed wastewater	7.19±0.45	1734±66	3888±155

11.1. Optimization of PAC dose for pre-treatment of WWAA

PAC was added in WWAA at different doses and allowed for 2 hrs for settling of sludge. At minimum dose of 1.25 m^3/day of PAC the COD reduction was 6.7% and colour reduction was 8.9%. At optimum dose of 7.5 m^3/day, COD and colour reduction were 55.6% and 92.0%, respectively. At maximum dose of 10 m^3/day of PAC, COD reduction was 83.7% and colour reduction was 96.9% **(Table 23, Figure 10)**.It shows that increasing the dose beyond 7.5 m^3/day, COD and colour reduction was not significant and commercial viable. Therefore, it was concluded that the PAC dose of 7.5 m^3/day is the optimum dose for pre-treatment of WWAA.

Table 23: Optimization of PAC dose for Pre-treatment of WWAA

PAC m^3/day (%)	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %	Treatment cost, Rs./m^3
-	1986	-	7640	-	-
1.25 (0.014)	1853	6.7	6958	8.9	1.5
2.50 (0.029)	1682	15.3	6200	18.8	3.0
3.75 (0.043)	1552	21.9	5116	33.0	4.5
5.00 (0.057)	1426	28.2	3596	52.9	6.0
6.25 (0.072)	1048	47.2	2287	70.1	7.5
7.50 (0.086)	881	55.6	610	92.0	9.0
8.75 (0.101)	650	67.3	425	94.4	10.5
10.0 (0.115)	410	79.4	237	96.9	12.0

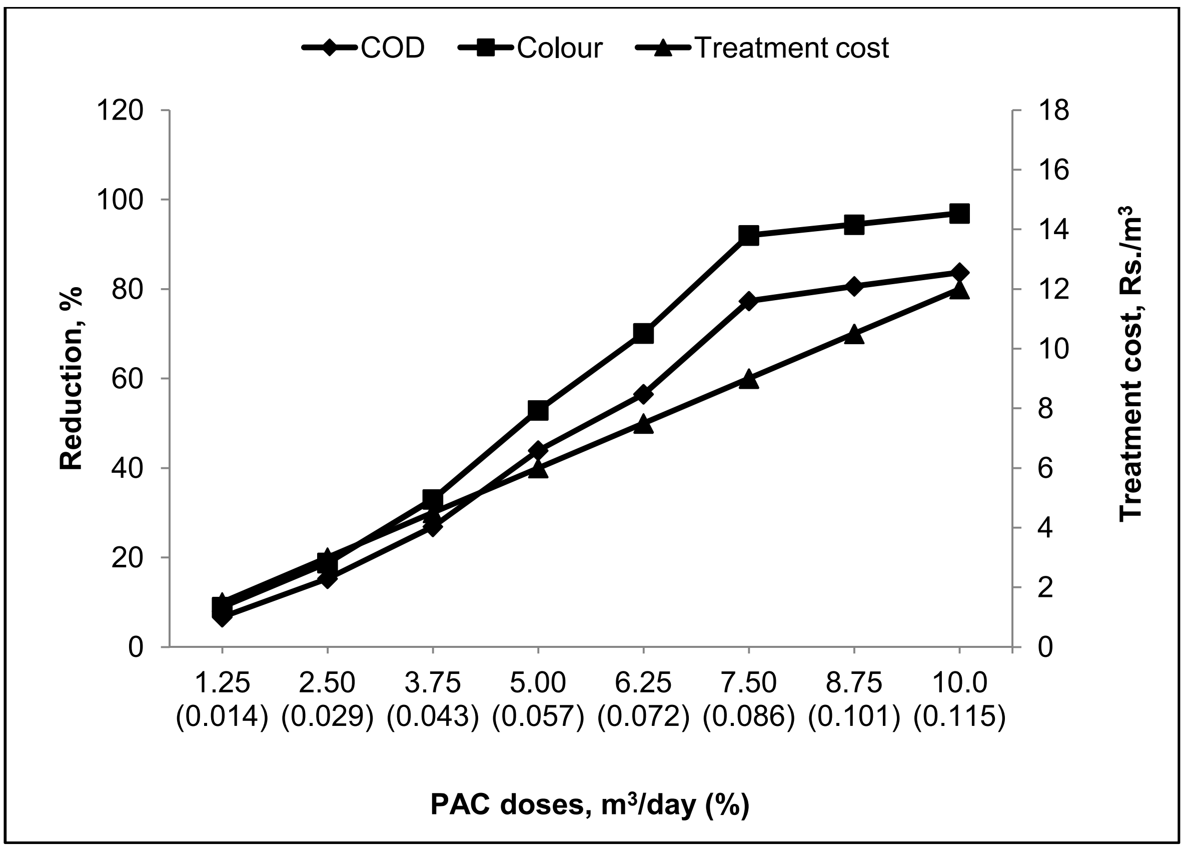

Figure 10: Graphical representation of effect of PAC dose for pre-treatment of WWAA

11.2. Mixing of mill wastewater and WWAA

The mill wastewater and WWAA were mixed in ratio of 7:3 and consider as Control feed F1. The feed was slightly basic in nature having COD 1734±66 mg/L and colour 3888±155 Pt-Co unit. 7.5 m^3/ day PAC was added in WWAA and after settling of sludge 3 parts of supernatant was mixed with 7 parts of mill wastewater: this mixed feed is considered as consider as PAC treated feed F3. The PAC treated feed with pH 6.94, COD 1371±42 mg/L and colour 2401±90 Pt-Co unit **(Table 24)**.

11.3.Effect of pre-treatment of WWAA (using PAC) on ASP performance

The Control feed F1 was treated in ASP reactor R-I at temp. 37.4±0.5°C and DO 1.0±0.2 mg/L was considered as Control. The same conditions maintained in another reactor R-II seeded with PAC treated feed F3. The MLSS, MLVSS and Organic content was maintained 3.84±0.40, 2.59±0.34 and 67.45±4.18 in control reactor R-I. The HRT was 10.0±0.21 in R-I. The COD reduction was 48.8% (887 mg/L) and colour reduction was 20.6% (3086 Pt-Co unit) in Control reactor ASP_{F1} **(Table 25)**. The COD reduction and colour reduction was achieved 61.8% (524 mg/L) and 44.8% (1326 Pt-Co unit) in ASP_{F3} (R-II) as given in **Table 26**. The feeding COD and colour plays a crucial role in biological system reduction. The efficiency of the biological treatment was found to increase with the reduction in initial COD and colour.

11.4. Effect of post-treatment of PAC to the ASP treated wastewater fed with feed F1 and F3

The samples collected after ASP from both of the reactors (ASP_{F1} and ASP_{F3}) for further treatment. The pH, COD and colour of sample collected from control reactor were 8.23, 887 mg/L and 3086 Pt-Co unit respectively. The PAC dose of 20 m^3/day was given in ASP_{F1} treated wastewater. The final pH after PAC treated wastewater was dropped to 5.0±0.1 with COD reduction 80.5% (339 mg/L) and colour reduction of 95.5% (175 Pt-Co unit) **(Table 26)**.

11.5. Effect of different doses of PAC on pre-treatment of WWAA (using PAC) on ASP performance

The PAC treated feed F3 with initial pH 6.94±0.11, COD 1371±42 mg/L and colour 2401±90 Pt-Co unit was treated with ASP_{F3} (reactor R-II). The MLSS, MLVSS and organic content were 3.65±0.74, 2.53±0.61 and 68.70±5.86 for reactor R-II. The HRT was 10.0±0.31 in R-II shown **(Table 25).** The ASP_{F3} showed 61.8% reduction in COD and 44.8% in colour. The ASP_{F3} treated wastewater samples were post-treated with two different doses of PAC to achieve the discharge parameters. The PAC dose 6.5 m^3/day showed the final pH 6.91 with COD value 361 mg/L and colour 377 Pt-Co unit. The PAC dose 8.5 m^3/day resulted in the final pH 6.51 with final COD of 205 mg/L and colour of 249 Pt-Co unit **(Table 27, Figure 11)**.

Table 24: Pre-treatment of WWAA wastewater with optimized dose of PAC 7.5 m^3/day

Parameters	pH	COD, mg/L	Colour, Pt-Co unit
Control Feed	8.16	1734	1371
PAC treated Feed	7.94	3888	2401

Table 25: Reactor parameters for both control feed and PAC treated feed

Reactors	MLSS,g/L	MLVSS,g/L	Organic content, %	HRT, hrs
ASP_{F1} (Control)	3.84±0.40	2.59±0.34	67.45±4.18	10.0±0.21
ASP_{F3}	3.65±0.74	2.53±0.61	68.70±5.86	10.0±0.31

Table 26: Effect of post-treatment of PAC to the ASP treated wastewater fed with feed F1

Samples	pH	COD, mg/L	Reduction, %	Colour, Pt-Co unit	Reduction, %
Feed F1 (control)	7.66	1734	-	3888	-
ASP_{F1}	8.23	887	48.8	3086	20.6
Post-treatment (with PAC - dose 20 m^3/day)	5.06	339	80.5	175	95.5

11.6. Characterization of final discharge

It was observed that colour, BOD and SAR were within discharge norms at total PAC dose of 20 m^3/day. At total PAC dose of 14 m^3/day, only pH and BOD were within limits. The split addition of PAC (total dose of 16 m^3/day) showed most of the parameters (except TDS) were within discharge norms i.e. pH 6.5, colour 249 Pt-Co unit, BOD 20 mg/L, TSS 23 mg/L and SAR 9.34 **(Table 28).**

Table 27: Effect of pre-treatment of WWAA (using PAC) on ASP performance

Samples		**pH**	**COD, mg/L**	**Reduction (w.r.t. inlet feed), %**	**Colour, Pt-Co unit**	**Reduction (w.r.t. inlet feed), %**
Feed F1 (control)		7.66	1734	-	3888	-
ASP_{F1}		8.32	887	48.8	3086	20.6
Feed F3 (pre-treated with PAC)		6.94	1371	-	2401	-
$*ASP_{F3}$		8.30	524	61.8	1326	44.8
Post-treatment of ASP_{F3} outlet with PAC	**dose 6.5 m^3/day**	6.91	361	31.1	377	71.6
	dose 8.5 m^3/day	6.51	180	60.9	249	81.2

*$ASP_{F3}$is the ASP treated wastewaters fed with feed F3 (WWAA treated with PAC).

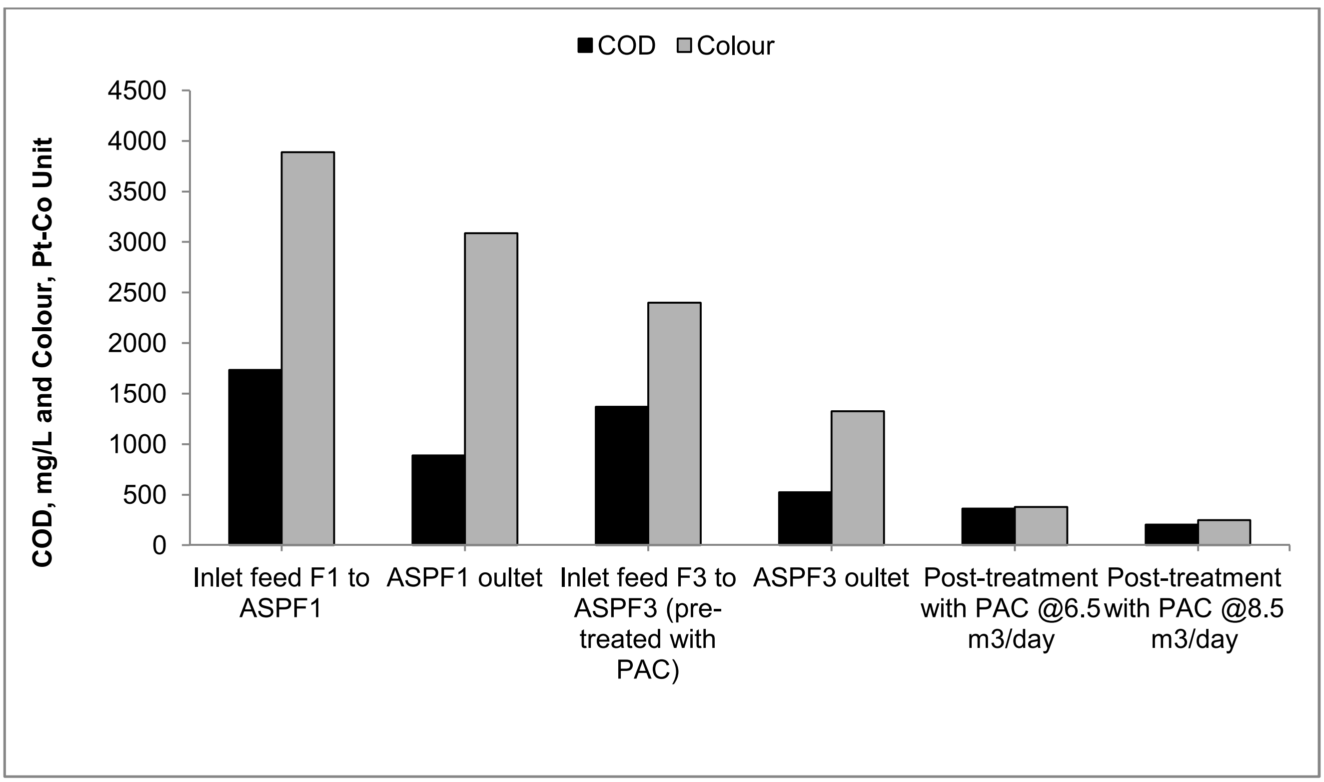

Figure 11: Graphical representation of effect of pre-treatment of WWAA (using PAC) on ASP performance

Table 28: Characterization of FDE with different PAC doses

Parameters	ASP_{F1}+post-treatment	ASP_{F3}+post-treatment	ASP_{F3}+post-treatment	Discharge norms as per recent norms
PAC dose during pre-treatment, m^3/day	-	7.5	7.5	-
PAC dose during post-treatment, m^3/day	20	8.5	6.5	-
Total dose of PAC, m^3/day	20	16	14	-
pH	5.1	6.51	6.91	6.5 - 8.5
COD, mg/L	339	180	361	200
Colour, Pt-Co unit	175	249	277	350
BOD, mg/L	24	20	26	20
TSS, mg/L	87	23	48	30
TDS, mg/L	3984	3296	3317	2100
SAR	9.43	9.34	12.1	10
AOX, mg/L	13.35	10.0	12.8	10

CHAPTER – 6

Handling and disposal of chemical sludge

12. Characterization of chemical sludge and saw dust

Proximate analysis of sludge and saw dust were shown in **Table 29.** The amount of sludge generated due to pretreatment of agro-based pulp and paper mill was approximately 2 kg/m^3. Due to its chemical nature, handling and disposal was the main concern. Use of this sludge as fuel might be an effective solution. As the combustion characteristics (GCV, Ash and volatile matter) of chemical sludge was found to be very less, to improve the combustion characteristics, this sludge was mixed in different ratio with auxiliary fuel such as saw dust having significant combustion value. These blended sludge derived fuel, in granulated form, is termed as briquette. When the proportion of sawdust was increased from 50% to 75%, the ash content was reduced from 27.1% to 13.1% successively. Whereas the volatile matter content increased from 61.9 to 71.5%. The remarkable changes were observed in GCV of fuel. The value increased from 3067 to 3598 kcal/kg, respectively. In comparison to saw dust, on increasing proportion of sludge from 50% to 75% combustion characteristics (GCV, Ash and volatile matter) were found to be decreased. Ash content was increased from 27.1% to 39.2%. Volatile matter was decreased from 61.9 to 49.5% and the value of GCV was decreased from 3067 to 2062 kcal/kg as shown in **Table 30, Figure 12.**

Table 29: Characterization of chemical sludge and sawdust

Parameters	**Unit**	**Sludge, OD basis**	**Saw dust, OD basis**
C	%	20.2	44.0
H		3.54	5.02
N		0.72	0.52
S		0.06	0.09
Ash		50.7	3.4
Volatile matter		44.2	80.3
GCV	kcal/kg	2013	4518

Table 30: Combustion properties of sludge and saw dust mixed in different proportions

Sludge : Saw dust	GCV (OD basis), kcal/kg	Ash, %	Volatile matter, %
1:1	3067	27.1	61.9
1:2	3348	18.7	68.1
1:3	3598	13.1	71.5
2:1	2576	35.1	56.2
3:1	2062	39.2	49.5

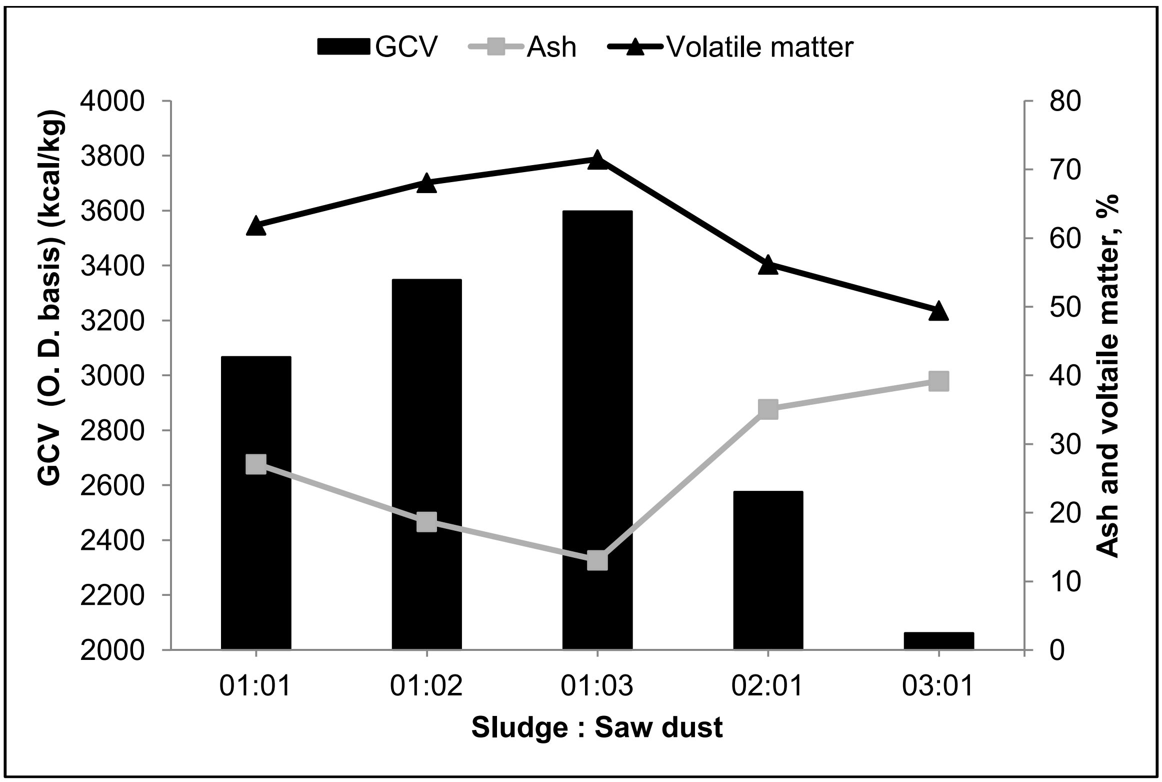

Figure 12: Graphical representation of combustion properties of sludge and saw dust mixed in different proportions

CHAPTER – 7
Enzyme study

13. Efficacy of enzyme for improvement of ASP performance

The Application of enzyme was reported to be effective for degradation of recalcitrant nature of compounds in symbiosis with biological treatment system of wastewater, which resulted in removal of colour, lignin, COD and AOX compounds. In our study, the laccase enzyme was procured from Punjab University, Chandigarh (Biotechnology department). The enzyme was isolated from fungal strain *Trametesbetulina* and the activity of Laccase enzyme was found to be 3000 IU/mL. The enzymatic treatment process comprised of enzyme (Laccase) and enhancer (H_2O_2).

13.1. Optimization of enzyme dose in batch study

The study was conducted for optimization of enzyme dose at batch scale with constant dose of enhancer (H_2O_2– 50ppm). It was found that at the given doses of enzymes (1.5 to 9.0 IU/mg of lignin) and enhance H_2O_2 (20 to 80 ppm) there was no significant reduction observed as represent **(Table 31 and Table 32)**. As no significant reductions were observed in batch study therefore evaluation of impact of enzyme laccase with microflora of activated sludge process has been studied in continuous bioreactors.

The running of different reactors including reactor - I as control (without addition of enzyme product and enhancer), reactor - II with only enzyme product (4.5 IU/mg of lignin), reactor - III with enzyme product (4.5 IU/mg of lignin) and enhancer (50 ppm) and reactor – IV with only enhancer (50 ppm) given in **Table 33**. The conditions of ASP reactors for optimized dose of enzyme and enhancer are given in **Table 34**. The results for first five days were taken as acclimatization period with chemicals (phase-I) and average of values for different parameters was taken for rest 10 days to evaluate the efficacy of enzyme system (phase-II).

The application of enzyme laccase was moderately effective for degradation of recalcitrant nature of compound during biological treatment which was clearly indicated due to good reduction of colour and COD in reactor-III as compare to reactor-I. The concentration of colour in feed was 3888±155 Pt-Co unit and removal of colour in all the bioreactors was consistent throughout the study. The reduction in colour in control reactor (R-I) was 22.6±2.5%, whereas in R-III was 34.7±1.5% where both enzyme and enhancer were added. The reduction in colour with only enzyme (R-III) was good. Application of enzyme was responsible for degradation of lignin and its derivative compounds in the wastewater which were further biodegradable during the biological treatment of the wastewater. The concentration of lignin in the feed was 136±9 mg/L and the reduction was 22.1±3.9% and 31.9±2.1% mg/L, respectively in wastewater from control reactor - I and reactor - III. Application of peroxide alone (R-IV) was not effective for oxidation of chromophoric groups and removal of colour was slightly higher than control reactor.

The concentration of soluble COD in the feed was 1734 mg/L during phase-II. As observed for colour, highest removal of COD was observed in R-III (53.2±1.9%) followed by RII (49.5±2.8%). The removal of COD in control was 46.6±3.2%, whereas it was similar to control in Reactor-IV as given in **Table 35**.

Table 31: Optimization of enzyme dose in batch study

Enzyme, IU/mg of lignin	5% H_2O_2, mg/L	pH	COD, mg/L	Red., %	Colour, Pt-Co unit	Red., %	Lignin, mg/L	Red., %
-	-	8.16	1734	-	3888	-	136	-
1.5	50	8.12	1729	0.3	3857	0.8	132	2.9
3.0	50	8.10	1724	0.6	3764	3.2	130	4.4
4.5	50	8.09	1687	2.7	3640	6.4	125	8.1
6.0	50	8.08	1687	2.7	3632	6.6	123	9.6
7.5	50	8.04	1685	2.8	3621	6.9	122	10.3
9.0	50	7.99	1682	3.0	3611	7.1	121	11.0

Table 32: Optimization of enhancer (H_2O_2) dose in batch study

Enzyme, (IU/mg of lignin)	5% H_2O_2 (mg/L)	pH	COD, mg/L	Red, %	Colour, Pt-Co unit	Red., %	Lignin, mg/L	Red., %
-	-	8.16	1734		3888	-	136	-
4.5	20	8.17	1722	0.7	3741	3.8	132	2.9
4.5	30	8.15	1710	1.4	3702	4.8	130	4.4
4.5	40	8.12	1702	1.8	3685	5.2	128	5.9
4.5	50	8.09	1687	2.7	3640	6.4	124	8.8
4.5	60	8.11	1684	2.9	3621	6.9	121	11.0
4.5	70	8.10	1681	3.1	3608	7.2	119	12.5
4.5	80	8.11	1679	3.2	3602	7.4	118	13.2

Table 33*:* Dosage of enzyme and enhancer in different bioreactors

Parameters	Reactor-I	Reactor-II	Reactor-III	Reactor-IV
Laccase, IU/mg of lignin	0	4.5	4.5	0
Enhancer, ppm	0	0	50	50

Table 34: ASP reactors for optimized dose of enzyme and enhancer

Parameters	Reactor-I	Reactor-II	Reactor-III	Reactor-IV
Temp., °C	37.5±0.26	38.5±0.12	38.0±0.21	37.80±0.24
HRT, hrs	9.24±0.35	9.41±0.59	9.37±0.94	9.28±0.84
DO, mg/L	1.09±0.24	1.00±0.14	1.07±0.15	1.04±0.16
MLSS, g/L	3.16±1.04	3.38±1.10	3.41±1.04	3.21±1.06
MLVSS, g/L	2.19±0.73	2.26±0.79	2.33±0.78	2.13±0.72
Organics, %	69.3±3.66	66.9±4.60	67.8±5.67	66.4±4.24

Table 35: Performance of different reactors

<table>
<tr><th colspan="2">Initial parameters of Feed</th><th>Red., %</th><th>Phase</th><th>Reactor-I</th><th>Reactor-II</th><th>Reactor-III</th><th>Reactor-IV</th></tr>
<tr><td rowspan="2">Colour, Pt-Co unit</td><td rowspan="2">3888±155</td><td rowspan="2">Colour,%</td><td>I</td><td>20.3±3.1</td><td>26.9±1.9</td><td>27.3±1.2</td><td>20.6±3.2</td></tr>
<tr><td>II</td><td>22.6±2.5</td><td>26.4±2.7</td><td>34.7±1.5</td><td>28.0±1.5</td></tr>
<tr><td rowspan="2">Lignin, mg/L</td><td rowspan="2">136±4.1</td><td rowspan="2">Lignin,%</td><td>I</td><td>20.0±1.7</td><td>25.7±5.9</td><td>26.3±6.2</td><td>21.3±2.4</td></tr>
<tr><td>II</td><td>22.1±3.9</td><td>29.1±2.8</td><td>31.9±2.1</td><td>21.2±2.9</td></tr>
<tr><td rowspan="2">COD, mg/L</td><td rowspan="2">1734±65.6</td><td rowspan="2">COD,%</td><td>I</td><td>48.4±2.9</td><td>52.8±0.9</td><td>50.1±6.7</td><td>45.2±2.9</td></tr>
<tr><td>II</td><td>46.6±3.2</td><td>49.5±2.8</td><td>53.2±1.9</td><td>45.0±2.6</td></tr>
</table>

CHAPTER – 8

Augmentation of bacterial consortia to ASP

14. Augmentation of bacterial consortia to ASP

After acclimatization of biomass, nitrogen fixing microbes (1 ml) with sucrose (1g) were added on the first day. After that only microbes were added. The results for first four days were taken as acclimatization period with microbes (phase-I) and average of values for different parameters was taken for rest 11 days to evaluate the efficacy of microbes addition (phase-II).

The pH of feed was set to 7.2±0.1 and average pH of outlet of R-I and R-II was 7.6±0.1 and 7.7±0.1.Similarly, average temperature varied from 37.0 to 38.2 ºC in all the reactors during the study. Dissolve oxygen was planned to set near to 0.8-1.2 and the same was maintained between 0.9-1.2 mg/L in all the reactors. HRT was 10.1±0.2 hrs in all the reactors. MLSS content in R-I, R-II and R-III was maintained 3.8±0.2, 3.9±0.2 and 4.0±0.3 g/l, respectively. The MLSS content was found to increase in Reactor-III where microbes were added.

Application of microbes was found effective for degradation of recalcitrant nature of compound during biological treatment which was clearly indicated due to higher reduction of color and COD in Reactor-III than control (where no N and P were added). The concentration of soluble COD in the feed was 1710±37 mg/L during phase-II. As observed for color, highest removal of COD was observed in R-III (53.8±2.7%) followed by R2 (51.0±1.1%). The removal of COD in control was 43.7±0.5% **(Table 36, Figure 13).** The concentration of color in feed was 3836±41 Pt-Co unit (PCU) and removal of colour in R-III was consistent throughout the study. The reduction in color in control reactor (R-I) was 19.9±0.5%, whereas the same in R-III was 28.7±2.3% where both microbes were added **(Table 36, Figure 14)**.The reduction in color with R-II (where N and P were added manually) was not good. Application of microbes was responsible for degradation of lignin and its derivative compounds in the wastewater.

Table 36: Effect of augmentation of bacterial consortium to reduce pollution load

	COD Reduction, %			Colour Reduction, %		
Days	**R-I**	**R-II**	**R-III**	**R-I**	**R-II**	**R-III**
Phase I (Acclimatization phase)						
1	47.2	50.0	46.3	18.4	20.0	7.1
2	43.7	49.6	45.5	18.9	22.0	10.7
3	43.6	48.9	42.1	20.7	20.2	12.3
4	44.4	51.5	42.3	19.8	21.1	17.1
Avg.	44.0	50.4	43.9	19.7	21.2	12.7
Std.	2.2	1.2	1.9	1.1	1.2	4.1
Phase II						
5	41.2	51.8	43.3	20.9	22.6	16.2
6	43.6	51.4	48.9	20.8	23.4	25.3
7	44.5	50.1	50.4	19.7	20.8	24.4
8	44.1	52.5	51.4	20.6	23.8	28.8
9	43.0	51.1	53.4	19.9	23.6	28.5
10	44.1	49.9	55.0	19.4	21.4	29.2
11	44.2	51.2	55.7	20.3	22.3	30.3
12	43.9	50.6	54.9	19.7	21.2	29.1
13	42.8	49.4	55.6	19.9	21.2	29.9
14	43.6	52.7	55.2	19.6	21.6	30.2
15	43.3	51.0	57.2	19.2	22.0	31.7
Avg.	43.7	51.0	53.8	19.9	22.1	28.7
Std.	0.5	1.1	2.7	0.5	1.1	2.3

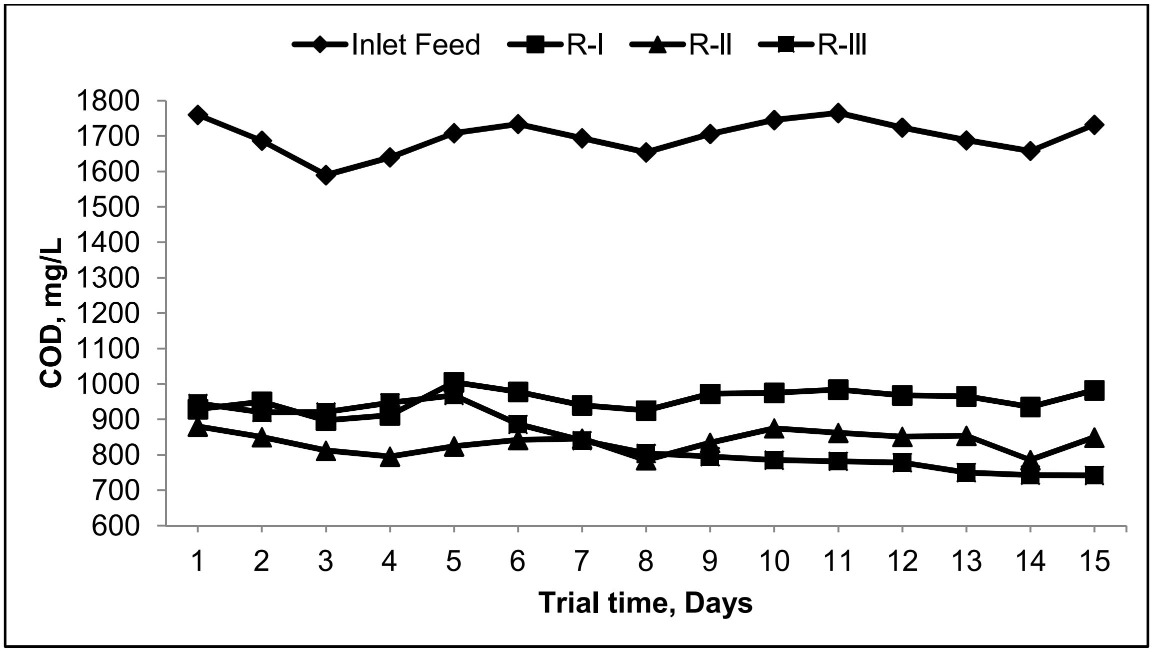

Figure 13: Graphical representation of day to day reduction of COD in different reactors

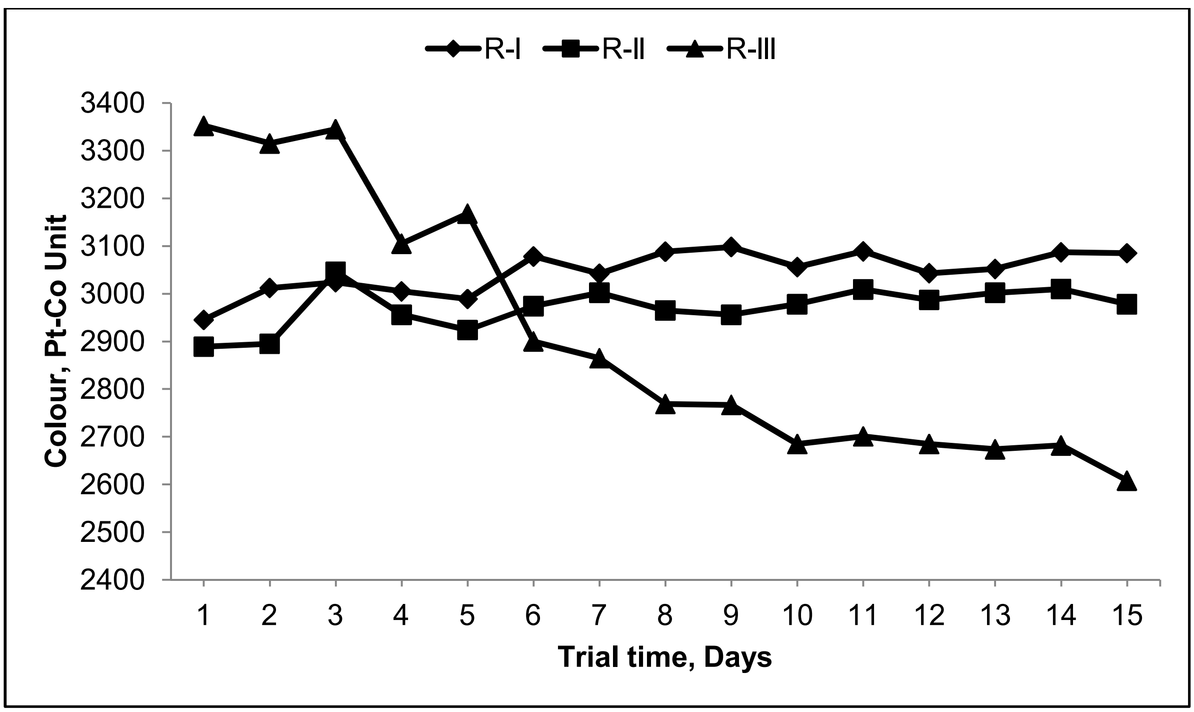

Figure 14: Graphical representation of day to day reduction of colour in different reactors

CHAPTER – 9

Demonstration of pilot scale (1.15 m^3/day trial at mill site)

Trial Date: May 01, 2018 to May 16, 2018

Site: An agro based paper mill

A pilot scale trial with wastewater treatment capacity of 1.15 m^3/day was conducted at a agro based paper mill site. The details of various components for pilot scale trial are summarized in **Table 37**. In the first two days the following set up for pilot scale trial was completed **(Figure 15 and 16)**.

Table 37: Details of various components for pilot scale trial

<table>
<tr><th>Particulars</th><th>Capacity</th><th>Purpose</th></tr>
<tr><td>Pre-treatment tank (1)</td><td rowspan="3">1000 L each</td><td>For the pre-treatment of anaerobically treated wet washing wastewater</td></tr>
<tr><td>Mixing tank (1)</td><td>For mixing 7 part of primary clarifier O/F (700 L) and 3 part of pre-treated anaerobically treated wet washing wastewater (300 L)</td></tr>
<tr><td>Feed tank (1)</td><td>For feeding the pre-treated wastewater (from mixing tank) to ASP as feed</td></tr>
<tr><td>ASP(1)</td><td>800 L</td><td>For activated sludge process (equipped with aeration, agitation and temperature controlling unit)</td></tr>
<tr><td>Clarifiers (2)</td><td>120 L each</td><td>To settle sludge present in ASP O/F</td></tr>
<tr><td>Sludge recycling system (1)</td><td>200 ml/min</td><td>For the recycling of sludge to maintain MLSS</td></tr>
</table>

The anaerobically treated wet washing wastewater was transferred directly to pre-treatment tank by attaching a pipeline with adequate valve to the sampling point available at the pipeline carrying wastewater. The pre-treatment was given to 1000 L anaerobically treated wet washing wastewater by using 3 L of PAC at a dose of 0.3%. The wastewater was properly mixed and kept for the settling of sludge in the tank for 2 hrs. After settling, 300 L of the supernatant of pre-treated wastewater was transferred via a pump to the mixing tank. 700 L of primary clarifier O/F from a pipe was also mixed in the same mixing tank. This properly mixed feed was transferred to feeding tank via a pump. ASP was connected to feed tank via a pump having a constant flow rate of 0.8 L/min to the ASP continuously (HRT 16 hrs.). The MLSS, DO and temperature of the aeration tank was maintained 2100±200 mg/L, 1.2±0.2 mg/L and 36±2°C, respectively during the trial. The O/F of the ASP was collected in the secondary clarifiers (HRT 2 hrs). The settled sludge was recycled back to ASP at a constant rate of 200±20 ml/ min.

This O/F of secondary clarifier was post-treated with PAC (0.1% dose). The COD, pH and MLSS analysis were carried out at mill site, while for color and BOD the samples were collected time to time and analyzed at ACIRD laboratory.

RESULTS

Pretreatment

It was observed that the average COD of anaerobically treated wet washing wastewater was reduced from 1884±42 mg/L to 858±39 mg/L with an average reduction of about 54.4±2.6%. The day to day analysis of COD is given in **Table 38 and Figure 17**. The average pH of anaerobically treated wet washing wastewater was 7.69±0.18, which was reduced to 6.43±0.04 after PAC pre-treatment.

ASP

When this pre-treated anaerobically treated wet washing wastewater was mixed with primary clarifier O/F, then the average COD of ASP inlet was found to be 1228±143 mg/L, which was lower than the average COD of mill ASP inlet (2028±59 mg/L). The average pH value of the mill secondary clarifier O/F was 7.17±0.04. In the first two days the average COD reduction was 16.0±1.3% (reduced from 1441±182 mg/L to 1212±172 mg/L) and for the next 6 days the average reduction was 36.0±3.0% (reduced from 1210±107 mg/L to 774±76 mg/L). During these 8 days the ASP was supposed to be in acclimatization phase. In the last 5 days, the average COD reduction was 48.4±1.0% (reduced from 1250±137 mg/L to 646±80 mg/L). The pH of secondary clarifier O/F was increased from 6.81±0.04 to 7.32±0.11 **(Table 39 and Figure 18)**.

Post treatment

The treatment was given at dose of 0.1% PAC based on the final pH value (~6.5) of the final discharge wastewater. It was observed that at 0.1% dose level, the COD reduction was 66.0±2.2% as given in **Table 40**. The results of different parameters viz. COD, BOD, colour, TSS, TDS and AOX of final discharge were lower than mill results. The data is summarized in the **Table 41**.

During the trial, we were able to run the ASP at reduced efficiency of around 48% due to some limitations. Based on laboratory data and mill data, the same was expected to be around minimum 60% **(Table 27)**, which is expected to further reduce the pollution load in post treatment also. In the lab scale reactors the pH of the outlet was around 8.3 due to higher degradation efficiency of ASP towards the degradation of lignin and its derivatives. After addition of 8.7 m^3/day PAC, the final pH was around 6.5 in laboratory results **(Table 27).** In case of pilot scale trial due to lower efficiency of the ASP, the pH of ASP outlet was on lower side (i.e. around 7.5) as compared to lab results.

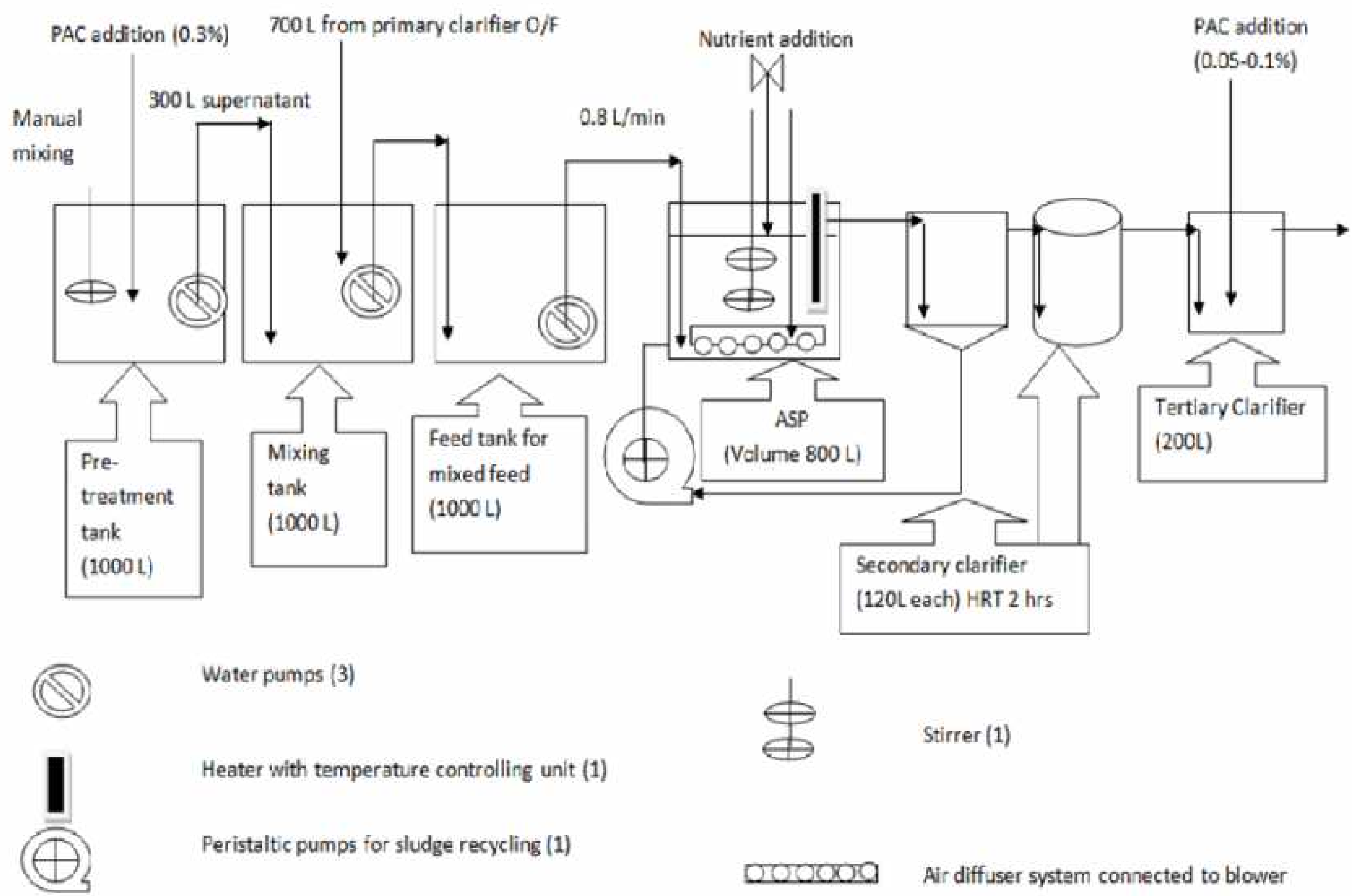

Figure 15: Sketch diagram of pilot scale wastewater treatment (1.15 m^3/d) demonstrated at mill site

Figure 16: Pilot scale (1.15 m^3/day)set up for wastewater treatment at mill site

Table 38: COD reduction after pre-treatment of anaerobically treated wet washing wastewater at PAC dose of 0.3%

Trial time, Day	Anaerobically treated wet washing wastewater		Pre-treated with PAC		COD reduction, %
	COD, mg/L	pH	COD,	pH	
1	1930	7.81	902	6.51	53.3
2	1919	7.71	892	6.42	53.5
3	1913	7.84	780	6.48	59.2
4	1880	7.91	805	6.42	57.2
5	1895	7.78	823	6.40	56.6
6	1876	7.24	856	6.40	54.4
7	1881	7.45	852	6.41	54.7
8	1910	7.80	885	6.45	53.7
9	1890	7.74	880	6.38	53.4
10	1906	7.64	857	6.43	55.0
11	1831	7.62	847	6.44	53.7
12	1773	7.71	920	6.48	48.1
13	1885	7.70	859	6.44	54.4

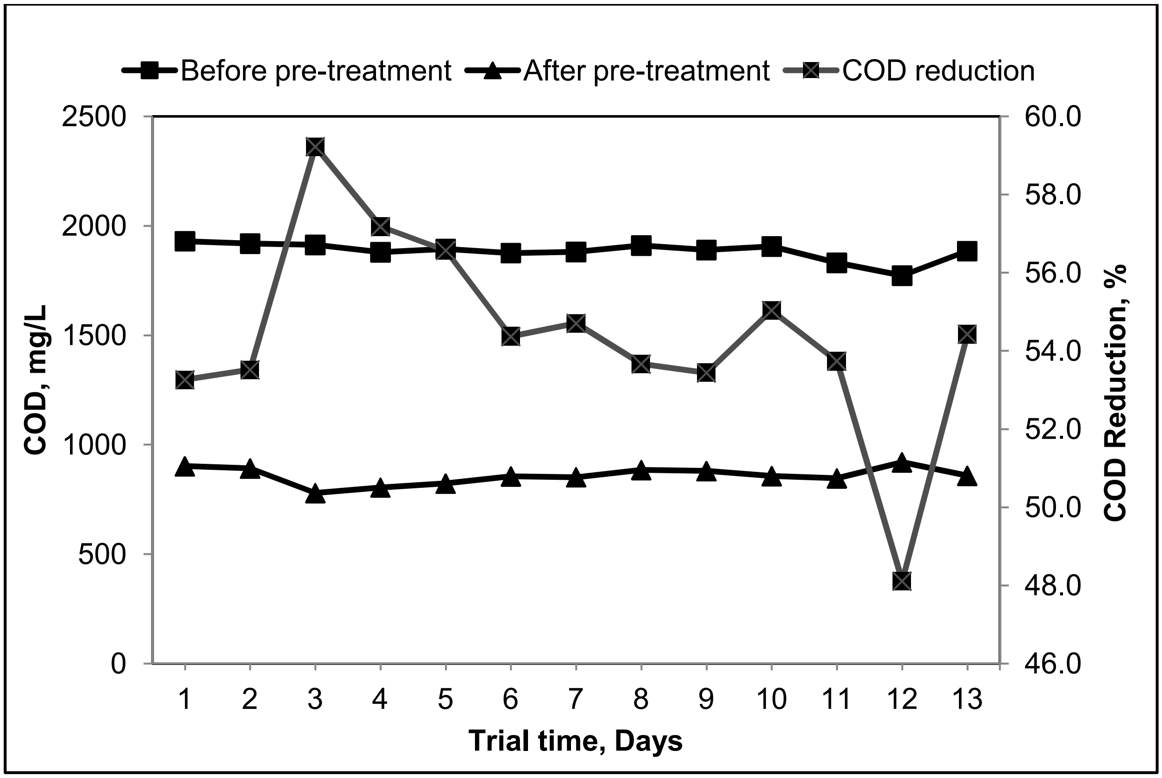

Figure 17: Graphical representation of COD reduction after pre-treatment of anaerobically treated wet washing wastewater

Table 39: COD reduction after ASP process using pre-treated mix feed

Trial time, Days	Mill results		Pilot trial results				
	ASP inlet		ASP inlet		ASP outlet		COD reduction, %
	COD, mg/L	pH	COD, mg/L	pH	COD, mg/L	pH	
1	2062	7.04	1569	6.78	1333	6.84	15.0
2	2026	7.16	1312	6.68	1090	6.91	16.9
3	2013	7.14	1320	6.65	880	6.96	33.3
4	2016	7.12	1258	6.69	806	7.01	35.9
5	2007	7.18	1274	6.78	745	7.10	41.5
6	2002	7.16	1167	6.81	778	7.12	33.3
7	2018	7.17	1019	6.91	649	7.21	36.3
8	2027	7.21	1220	6.84	788	7.16	35.4
9	2078	7.22	1157	6.78	579	7.40	50.0
10	2017	7.21	1130	6.76	587	7.30	48.1
11	2011	7.14	1165	6.85	601	7.23	48.4
12	1932	7.18	1422	6.80	753	7.19	47.0
13	2192	7.11	1374	6.84	708	7.46	48.5

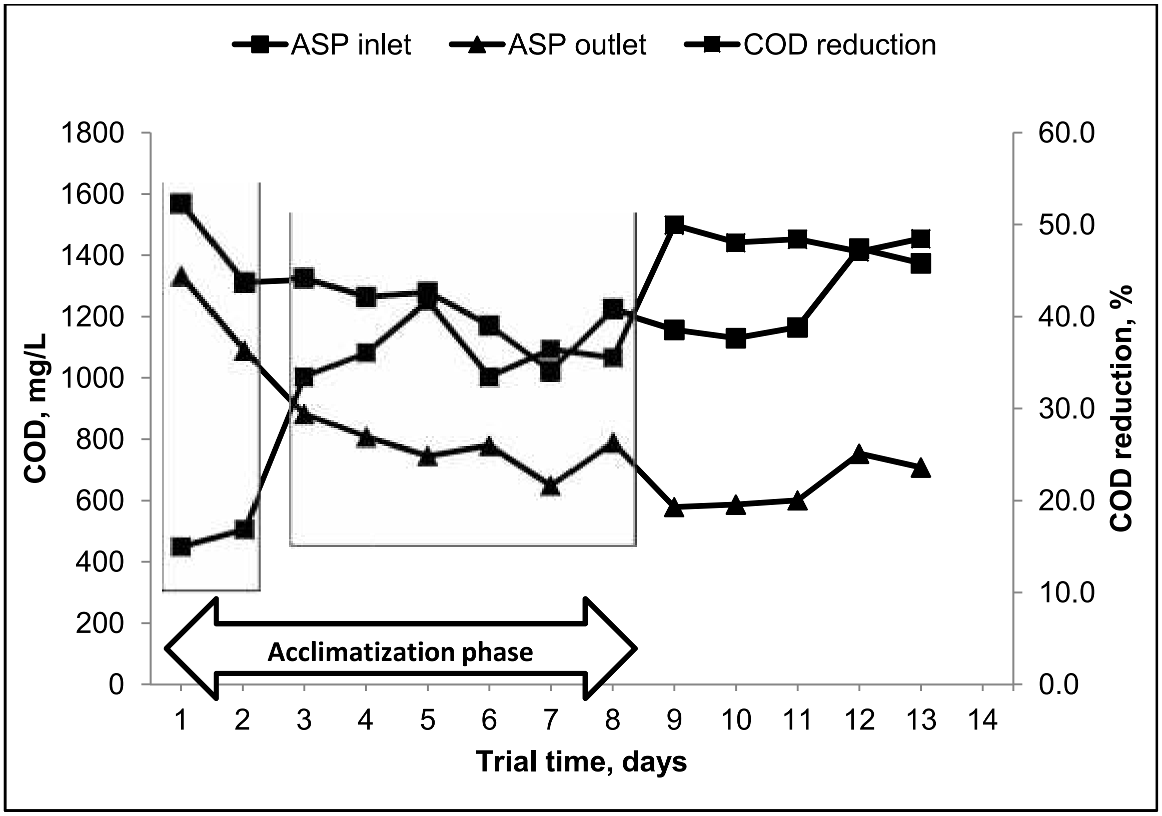

Figure 18: Graphical representation of COD reduction after ASP process using pre-treated mix feed

Table 40: Results of post-treatment of PAC at the dose of 0.10%

Trial time, Days	PAC dose, %	Post-treatment, inlet		Post-treatment, outlet		COD reduction, %
		COD, mg/L	pH	COD, mg/L	pH	
10	0.10	587	7.30	198	6.56	66.3
11	0.10	601	7.23	206	6.53	65.7
12	0.10	753	7.19	240	6.50	68.1
13	0.10	708	7.46	232	6.63	67.2

Table 41: Summary of pollution load of different streams in results of pilot scale and mill

Parameters	Pilot trial results (Last 4 days)				Mill Results
	Pre-treatment	Mixed feed	ASP outlet	Post-treatment	Final discharge (after PAC treatment)
COD	857	1130	587	198	271
	847	1165	601	226	248
	920	1422	753	240	272
	859	1374	708	232	278
Avg.	871±33	1273±147	662±81	224±16	267±11
BOD	57.1	405	-	19.1	22
	55.2	401	-	21.9	24.2
	62.4	486	-	22.7	25.1
	59	476	-	20.8	24.5
Avg.	58.4±3.1	442±45		21.1±1.3	24.0±1.2
Colour	915	1259	1606	313	407
	907	1295	1675	335	372
	976	1586	2012	359	408
	905	1524	1965	346	417
Avg.	926±34	1416±163	1815±204	338±17	401±17
TSS	166	81.3	251	22.9	49.8
	158	74.4	243	24.6	46.5
	181	92.9	299	27.6	48.9
	159	82.3	263	26.2	49.6
Avg.	166±11	82.7±7.6	264±25	25.3±2.0	48.7±1.3
TDS	4626	3870	3446	3068	3931
	4536	3659	3265	3276	3682
	5085	3865	3215	3024	3629
	4665	3925	3521	3215	3858
Avg.	4728±244	3830±117	3362±145	3146±119	3775±124
AOX	-	32.1	23.1	9.13	10.1
	-	33.1	22.6	9.08	10.3
	-	32.6	23.8	9.53	10.5
	-	31.8	22.4	9.47	9.56
Avg.		32.4±0.5	23.0±0.6	9.30±0.20	10.1±0.4

CHAPTER – 10
Validation of findings by CPPRI

Validation Date: June 09, 2018 to June 28, 2018

During the project work, different studies were carried out by ACIRD to treat the wastewater through biochemical method. Different oxidizing agents such as PAC, Alum, Lignoclean-18, Lignoclean-22, Ozone and H_2O_2, were used for treatment of wastewater. Through use of different chemicals, results revealed that PAC can be used for the treatment through split addition (initially for treatment of effluent generated through wet washing after anaerobic treatment followed by post treatment after ASP) and found most effective for wastewater treatment due to its low cost in comparison to others chemicals and same was used for pilot scale trial. The trial was conducted by ACIRD in an agro based pulp and paper from May 01-16, 2018.

The results of the pilot trial were discussed with CPPRI scientists and it was decided to have validation of these results by CPPRI. The results of the study are given below in **Table 42.**

Table 42: Results of pre-treatment of wastewater Wet Washing After Anaerobic (WWAA) with PAC

Parameters	Lab results (ACIRD)	Lab results (CPPRI)
Pre-treatment of WWAA		
Initial COD, mg/L	1428±56	1440
Final COD, mg/L (Reduction %)	692±24(51.5±1.6)	734

After Pre-treatment of PAC, the effluent was mixed with mill effluent in a ratio of 3:7 (the same ratio is being used at mill) and results were summarized in **Tables 43, 44**.

Table 43: Results of mixed feed(3-part WWAA after pre-treatment with PAC and 7-part Mill effluent) to ASP inlet

Parameters	Lab results (ACIRD)	Lab results (CPPRI)
COD, mg/L(Mixed feed to ASP inlet)	1060±36	1008
COD, mg/L (ASP outlet) **(Reduction %)**	372±15 (64.9±2.1)	365

Table 44: Results of post-treatment of ASP outlet with PAC

Parameters	Mill results	Lab results (ACIRD)	Lab results (CPPRI)	Discharge Norms (as per recent norms)
COD, mg/L	267	192	187	200
BOD, mg/L	24	18	16	20
Colour, Pt-Co unit	401	232	240	350
TSS, mg/L	48.7	21	18	30
TDS, mg/L	3775	3250	3188	2100
AOX, mg/L	10.1	8.01	7.92	10

Comments by CPPRI:

1. The experiments with PAC were carried out at ACIRD, Yamuna Nagar using wet washing effluent after anaerobic treatment, mixed effluent (3-part WWAA after pre-treatment with PAC and 7-part Mill effluent) inlet to biological treatment (ASP) and after biological treated (ASP) outlet effluent.

2. The treated effluent samples were analyzed at CPPRI and ACIRD.

3. The results of analysis at CPPRI & ACIRD are more or less comparable for different pollutional parameters.

CONCLUSIONS

The effect of enzyme and microbes has been studied in symbiosis with micro flora of activated sludge process to increase its efficiency. The study revealed that enzyme laccase was moderately effective in comparison to microbes for degradation of recalcitrant compound during biological treatment of wastewater.

Different chemicals and oxidizing agents such as PAC, Alum, Lignoclean-18, Lignoclean-22, Ozone and H_2O_2, were used for treatment of the wastewater. PAC was found to be effective for wastewater treatment due to its low cost in comparison to others.

Based on the research work carried out in this research work, it was concluded that spilt dosing of PAC (total dose 16.2 m^3/day) used for pre-treatment of anaerobically treated wastewater (using 7.5 m^3/day PAC) followed by post-treatment (using 8.7 m^3/day PAC) is effective to reduce the pollution load significantly by using about 20% less PAC (cost saving Rs. 12000/day), as the mill is currently using 20 m^3 PAC per day. A pilot scale trial (1.15 m^3/day) was successfully demonstrated for 4 days (after acclimatization of ASP). The results were in accordance with laboratory findings. All the values of different parameters (except TDS) of final discharged wastewater were within the discharge limits.

The treatment cost with PAC will be Rs. 5.5/m^3 of wastewater, which is the lowest in all the given treatment. Although, ozone treatment cost was Rs. 4.9/m^3 but COD value was found higher than the discharge norms. This treatment cost is for two stage treated wastewater after ASP. The treatment efficiency with respect to inlet feed for ozone treatment was not significant. Ozone treatment also requires capital investment for ozone generation. The Alum and Lignoclean were found to be effective to meet the discharge norms but at a higher cost of Rs. 7.1/m^3 and 14.3/m^3, respectively **(Table 45)**. During the treatment of PAC, chemical sludge was generated so its handling and disposal was the main concern .Use of this sludge as fuel might be an effective solution. Proximate analysis revealed that its combustion efficiency was less effective so the study was done to improve the combustion value of the same by mixing with saw dust. Appreciable result was found. The result indicate that mixing of saw dust improve the burning efficiency from 2007 to 3567 kcal/kg.

Table 45: Comparison of treatment cost for various biochemical treatments for reduction of pollution load

Chemicals	Dose per m^3		COD, mg/L	Red., %	Colour, Pt-Co unit	Red., %	Cost Rs /m^3
	Coagulant/ chemical	Flocculant					
PAC	1.84 kg	-	180	88.6	249	92.8	5.5
Alum	0.83 kg	5.17 g	198	87.4	212	92.6	7.1
Lignoclean-18	0.70 kg	1.00 g	187	88.1	147	94.9	14.3
Lignoclean-22	0.40 kg	3.00 g	311	80.3	572	80.3	16.8
Ozone	49.0 g	-	303	80.8	254	91.1	4.9
H_2O_2	0.10 kg	-	679	56.9	1643	42.6	7.0

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