STUDIES ON RELEASE OF ADSORBABLE ORGANIC HALIDE (AOX) FROM PULP & PAPER INDUSTRY THEIR TOXICITY & CONTROL

BY

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Akash Pandey

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DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

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Name

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled ***"STUDIES ON RELEASE OF ADSORBABLE ORGANIC HALIDE (AOX) FROM PULP & PAPER INDUSTRY – THEIR TOXICITY & CONTROL"*** submitted by **AKASH PANDEY** to **UNIVERSITY OF PETROLEUM & ENERGY STUDIES** for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by him under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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EXECUTIVE SUMMARY

CHAPTER 1 - INTRODUCTION

The first chapter comprises the history of pulp and paper manufacture in India, the number of mills producing the papers, categorization of mills on the basis of raw material, paper making process. Different process like raw material preparation, pulping, bleaching, stock preparation and paper making process are briefly discussed in this chapter. Other process which are the part of paper mills like chemical recovery & effluent treatment plant are also discussed. In this chapter also discussed the technological & environmental issues before Indian pulp and paper industry. And lastly the main objective of this research studies, release of Adsorbable Organic Halide (AOX) in the pulp and paper industry and their impacts are discussed.

On the basis of their end product, pulp & paper mills are classified in to writing & printing paper mills, newsprint mills & rayon grade mills. Indian pulp and paper mills are also classified on the basis of their raw material viz. wood based and agro based mills. In India the mixed raw material are used for the paper making process. Pulping is the process of converting wood or non wood material to separated pulp fibers for paper making. Two type of pulping process employed i.e. sulfate/ kraft process (using NaOH & Na2S) & soda process for producing variety of paper. The bleaching of pulps are done by different sequences generally CEH stages. The major portion of lignin was usually removed in subsequent bleaching stage. During bleaching large amount of effluent generate collectively known as Bleach Plant Effluent and bleach effluent contains toxic compounds known as Adsorbable

Organic Halide (AOX). The environmental hazards of bleach plant effluent are considered related to the use of chlorine containing bleach chemicals especially molecular chlorine.

After bleaching of pulp, it goes to stock preparation and paper making section. Stock preparation is an important & integral part of paper manufacturing which influence the quality of finished paper.

These AOX compounds are reported to be carcinogenic and bioaccumulable in nature and persist in environment for a long time. The consequences of AOX discharged in mill effluents were recognized by developed countries when high concentration of these compounds were detected in fish fat stocks receiving bleach plant effluent. These compounds are reported to have tendency to accumulate in fish & are responsible for acute toxicity.

The environmental concern of AOX has been recognized by CPCB & MoEF through formulation of Charter on Corporate Responsibility for Environment Protection (CREP) under which the mills have been asked to adopt necessary measure to reduce the level of AOX.

CHAPTER 2.0 - LITERATURE REVIEW

Chapter 2.0 comprises with exhaustive literature survey carried out on historical background and manufacture process of pulp and paper mills in India and abroad, nature and origin of AOX compounds, mechanism of generation of AOX compounds, environmental impact etc , latest technological developments in pulp & paper industry for reducing AOX .

CHAPTER 3.0 - CHARACTERIZATION OF BLEACH PLANT EFFLUENT

The chapter no. 3.0 include characterization studies of bleach plant effluents generated in laboratory as well as collected from Indian pulp and paper mills. The studies were carried out as per "Standard methods for the Examination of Water and Wastewater" (APHA), while AOX was determined as per DIN 38409 Tail 14 AOX procedure. Methods. The complete procedure of collection and preservation methods of effluents samples, determination procedure of major pollutional parameters including AOX is described in the chapter.

CHAPTER 4.0 - TOXICITY EVALUATION OF BLEACH PLANT EFFLUENT

Chapter 4.0 include toxicity assessment of different bleach plant effluent collected from pulp and paper mills using fish toxicity bioassay and microtox toxicity tests . The tests indicate that E-stage bleach effluent were more toxic than the other stage effluent. Bleach plant effluent collected from Agro based mills were more toxic than the wood based mills.

CHAPTER 5- CONTROL MEASURES FOR REDUCTION OF AOX

In the chapter 5, different treatment studies for reduction of AOX is studied. This chapter included the chemical treatment studies with main focus on evaluation of combination of chemicals easily available in the mills, optimization of dosages, optimization of treatment conditions to reduce the level of toxic material in bleach plant effluent Impact of physical treatment like carbon adsorption & thermal treatment as well as Biological treatment is covered under this chapter. Other in-house options to control the AOX level have also been explored like use of some recycle fiber in place of bleached pulp, optimization of pulping process to reduce the Kappa No. etc.

CHAPTER 6.0- RESULTS & DISCUSSION

The chapter 6.0 summarizes and interprets the results of various experimental studies carried out related to characterization of bleach plant effluent collected from agro & wood based mills, toxicity of bleach plant effluent, performance efficiency of chemical and physico – chemical & biological treatment studies in context of reduction of AOX and other pollution load.

The pollution load in the small pulp and paper mills using agro based raw material is higher than large pulp and paper mills using wood based raw material. This is due to absence of chemical recovery system in most of the small agro based mills. As a result these mills produce pulp of high kappa number and consequently high quantity of chlorine or chlorine based chemicals are used in pulp bleaching to achieve desired brightness target level resulting in high level of AOX & not any controlled over chemical consumption for bleaching of pulp.

Results of Toxicity studies of E-stage bleach plant effluent shows that it is highly toxic than the other stage effluent and due to this E-stage effluent needs to be treated before being discharged to the aquatic environment.

Reduction in toxicity of bleach plant effluent is also observed after chemical treatment. This shows that chemical treatment is good technique to reduce the toxicity of bleach plant effluent up to that level which will not harm to aquatic organisms.

The reduction in AOX including COD, and Color obtained by use of carbon adsorption technique were quite encouraging but the process have some limitations like huge volume of the effluent to be treated, regeneration cost of activated carbon is more.

The reduction in AOX was about 67-70% after using lime and alum prior to biological treatment while the 51-56% reduction in AOX was achieved without using lime & alum.

The reduction in AOX through biological system is less in small scale agro based mill due to less activity of biological process.

CHAPTER 7.0 - CONCLUSION & RECOMMENDATIONS

The chapter concludes with highlighting the three way approach to control AOX viz - In house Control Measures, End of pipe(EoP) treatment, Integrated Approach (combination of In-house & EoP Treatment). The in house approach include - Optimization of process operations, Producing low kappa pulp below 20, Improved efficiency of pulp washers to ensure low COD carry over, oimization of fiber furnish , increased used of RCF in fiber furnish , control of spillages of bleach plant effluent through setting up of collection tanks & seal pits, etc, segregation of highly polluted streams and less polluted streams for appropriate treatment, expansion of pulp mill capacity, etc.

CHAPTER 8- REFERENCES

It includes the list of literature / references cited related to Adsorbable Organic Halides formation, generation, level of AOX in developed and in Indian Pulp & Paper Mills, their environmental and health impact, control options etc.

CHAPTER -1.0

INTRODUCTION

1.1 INDIAN PULP & PAPER INDUSTRY - AN OVERVIEW

Pulp and paper industry is one of the oldest industries in India. As per the official records, the first paper mill was started in 1812 in Serampore (West Bengal) which was based on the grasses and jute. Mechanized technologies for large scale paper manufacturing were started in India in early 1905. At that time raw materials for paper making underwent a number of changes and over a period of time, besides bamboo and wood, other non conventional raw materials were identified and today bagasse, wheat straw, rice straw are being used for manufacturing of paper. At the time of independence there were less than 20 mills in India with total annual capacity of 100,000 tons. Though the initial years were not very encouraging due to lack of demand as well as political turmoil at national & global level, a few new mills were established between 1857- 1887. The real growth took place during the formative years of independent India. Started with imported pulp, bamboo became the main source of paper making fibers subsequently after development of technology of pulp making from bamboo. Since then, the paper industry has made a gradual progress along with certain hiccups / setbacks in between as an impact of global & national economic & political conditions. Today the industry occupies an unique position in Indian economy and is marked as a sector having mills of wide range of scale of operation, using diverse raw material for pulp & paper making and having low (with few exceptions) technological & environmental status in general. Today the total number of pulp & paper mills in the country are estimated to be around seven hundred & fifty nine (759) equivalent to an installed capacity of over 12.7 million tonnes which is likely to increase over 22 million tonnes by the year 2020 . Out of the total installed capacity about 1.30 million tonnes is idle (not in operation / closed).The present level of paper consumption in India is around 11.15 million tones which makes the per capita consumption of the country a meager 9.3 kg as against 332 kg in USA and world average of 54 kg. With such lower per capita consumption the industry has a greater scope of further growth. The industry offers employment to more than 0.3 million people directly and about 1 million people indirectly.

1.2 CATEGORISATION OF PULP & PAPER MILLS

The Indian pulp and paper industry is categarised into wood / forest based, agro based and waste paper based with the wood/ forest based accounting for 37 %, agro based 33 %, and waste paper based 30 % of the installed capacity given in **Fig- 1.1.** A brief account of the various process operation followed in paper mills is discussed. The pulp and paper mill is classified on the following basis in **Table- 1.1.**

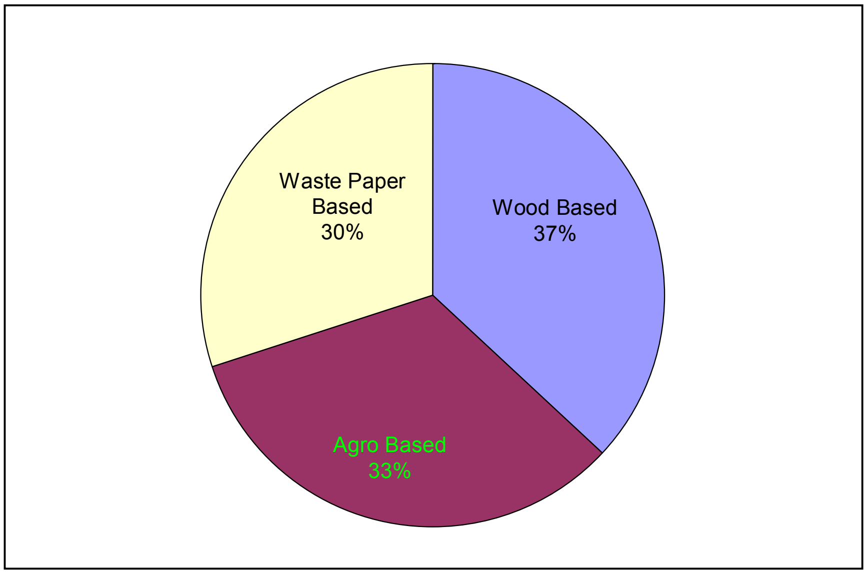

Fig 1.1 - General Structure of Indian Pulp & Paper Industry

TABLE- 1.1

BASIS OF CLASSIFICATION OF IINDIAN PULP & PAPER MILLS

Classification Basis		
Raw material Used	**Scale of Operation, (tonnes per day)**	**End products**
• Wood based • Agro based • Recycled Fiber based	• Large (Above 100) • Medium (30-100) • Small (5-30)	• Writing & Printing, Newsprint, Rayon grade pulp. • Writing & Printing, Newsprint, Packaging paper etc. • Writing & Printing, Newsprint, Packaging paper etc.

1.3 PAPER MAKING PROCESS

The paper making process has a group of processes which is in general given in the **Fig 1.2.**

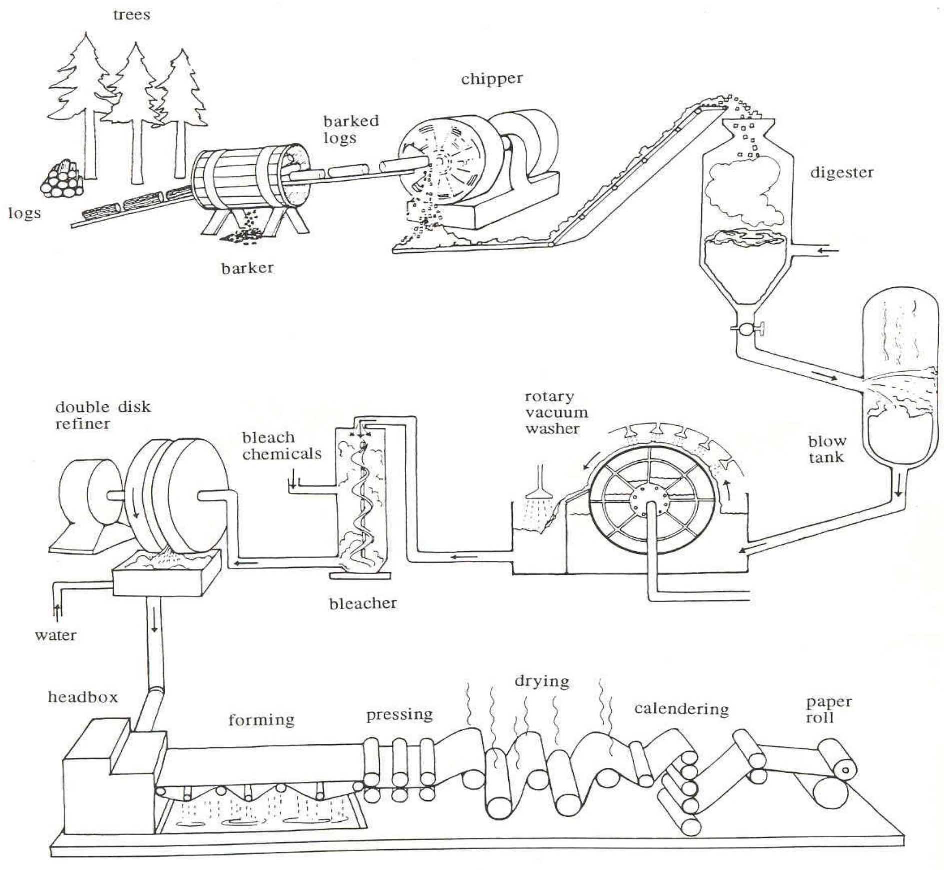

Fig 1.2 - Schematic of Pulp and Paper Manufacturing Process (TAPPI)

A brief account of the various process operations followed in Indian Pulp and Paper mills are as under:

1.3.1 RAW MATERIAL USED

Wood Based Large Mills

The major fiber sources for pulp & paper making include **bamboo and mixed hardwoods from forest fellings, Eucalyptus, Casurina , Poplar , Bagasse, RCF etc.**

Agro Based Small mills

These mills use mainly agro residues such as **bagasse, wheat straw, rice straw, grasses, sarkanda, jute, cotton linters** etc. which are available seasonally.


Bagasse Bamboo Hardwood

Kenaf Wheat straw Recycled fiber

Fig 1.3 - Major Raw Material Used by Paper Industry

1.3.2 PULPING PROCESS

Wood Based Large Mills

Almost all mills employ **sulfate/ kraft process (using NaOH & Na_2S with sulfidity level 18-25%)** for producing writing and printing paper. Depending upon the capacity, mills employ blow heat recovery system by which waste heat recovery is accomplished alongwith defiberation of the cooked material. Very few mills have continuous digesters or employ modified pulping process to reduce kappa number of pulp to about 18. **Rayon grade mills** employ prehydrolysis process before sulfate process to produce unbleached pulp of kappa number around 10-12 while newsprint mills use both chemical (sulfate) & mechanical pulping process (CMP & TMP). **Newsprint mills** use major proportions of mechanical pulp in the fiber furnish. The kappa number of unbleached pulp produced in most of the mills is more than 22 for producing writing and printing paper and major part of lignin is still removed in subsequent bleaching stage. Recycled fiber is usually processed in hydra pulper followed by deinking.

Agro Based Small Mills

Almost all agro based mills employ **soda process** for producing variety of paper. Most of the mills use multiple **batch digesters** of low capacity. Recently some mills have installed **continuous digester**. These mills normally produce pulp of high kappa number as high as 25-30 due to some economic reasons, resulting in use of high level of elemental chlorine and hypochlorite leading to generation of high level of pollution loads in effluents. However, the mills having chemical recovery system are normally producing pulps of kappa number 20-25 for production of writing and printing paper.

1.3.3 PULP WASHING

Wood Based Large Mills

Most of the pulp mills normally use brown stock washers for washing of pulp using counter current washing practices. Recent trends include Belt washers, Twin roll Press, displacement drum etc

Agro Based Small Mills

Most of these mills are having 2-3 stage brown stock washers for pulp washing but in most cases these washers are overloaded. Some mills are still using potcher washing system which requires large volume of water compared to BSW. Since most of the agro based mills are not equipped with chemical recovery system, so the concept of counter current washing system is not strictly followed, which results in generation of high volume of black liquor at very low concentration some time below 1-2% solids. Recently some mills installed twin drum washer prior to brown stock washer to extract the black liquor to the maximum extent.

Oxygen Delignification

Oxygen delignification process is a well established technology used to treat unbleached pulp to reduce kappa number before bleaching of pulp in order to reduce chlorine demand. Increasing number of large mills are going for oxygen delignification with main objective to reduce kappa no & consequently chlorine consumption. Small mills have not adopted it yet due to low scale of operation & high capital investment required

1.3.4 BLEACHING PRACTICES

Wood Based Large Mills

Most of the mills are having conventional bleaching sequence (CEHH, CEpHH) but few are switching over to ECF Bleaching to improve the quality of pulp & reduce pollution loads in bleach plant effluent. Newsprint mills generally use hydrogen peroxide for bleaching of mechanical pulp and conventional bleaching techniques for chemical pulp. Rayon grade pulp is generally bleached using elemental chlorine, sodium hypochlorite followed by chlorine dioxide to produce pulp of higher brightness.

Agro Based Small Mills

Most of the mills are employing conventional bleaching process i.e. CEH / CEHH or only hypochlorite in two or three stage. The consumption of chlorine in these category of mills is comparatively higher.

The following chemicals are used in the pulp and paper mills for bleaching of pulps to increase the brightness and given in **Table 1.2 & 1.3.**

TABLE –1.2

CHEMICALS USED IN BLEACHING OF PULPS

Oxidants	Form	Advantages	Disadvantages
Chlorine	Gas	Effective, economical delignification,	Can cause loss of pulp strengths if used improperly. Orgaanochlorine formation.
Hypochlorite	Ca $(OCl)_2$ NaOCI solution – 40 gpl. As Cl_2.	Easy to make and use.	Can cause loss of pulp strength if used improperly. Chloroform formation.
Chlorine Dioxide	7-10 gpl $Cl0_2$ solution in water	Achieves high brightness without pulp degradation. Good particle removal.	Must be made on site. Expensive. Some orgaanochlorine formation.
Oxygen	Gas used with NaOH solution	Low chemical cost. Provides chloride-free effluent for recovery	Used in large amounts requires expensive equipment. Can cause loss of pulp strength.
Hydrogen peroxide	2-5% solution	Easy to use low capital cost	Expensive, poor particle bleaching
Ozone	Gas in low concentration in oxygen	Effective, provides chloride- free effluent for recovery	Expensive, Degrades pulp. Poor particle bleaching.
Reluctant Hydrosulfite (for mechanical pulps only)	Solution of Na_2S_20H or made onsite from NaBH4 solution plus SO_2)	Easy to use. Low capital cost	Decomposes readily. Limited brightness gain.
Alkali Sodium Hydroxide	5-10% NaOH solution	Effective and economical	Darkens pulp

TABLE-1.3

BLEACHING CHEMICALS AND PROCESS SHORT HAND NOMENCLATURE

Stage	**Chemicals Used**	**Symbol**
Chlorine	Cl_2	C
Alkaline extraction	NaOH	E
Hypochlorite	NaOCl+NaOH	H
Chlorine Dioxide	ClO_2	D
Peroxide	Na_2O_2+NaOH	P or P/E
	H_2O_2+NaOH	P or P/E
Oxygen	O2+NaOH	O
Chlorine/ ClO_2	Cl_2/ClO_2	C_D
Sequential Bleach	ClO_2/ Cl_2	D/C
	Cl_2/NaOCl+NaOH	C/H
	ClO_2/NaOCl+NaOH	D/H
Mixed Bleach	Cl2+ClO2	C+D
Low level chlorine	Cl_2	(C)
Gas phase bleaching	Cl_2	C_g
	ClO_2	D_g
Ozone	O_3	Z
Acid	CH_3CO_3H (example)	A

1.3.5 STOCK PREPARATION & PAPER MAKING PROCESS

Stock preparation is an important & integral part of paper manufacturing which influence the quality of finished paper. Around 10-15% of various chemicals are used in combination for development of physical & optical properties of paper. The average capacity of paper machines in large mills is about 14000 t/ annum. Thus even the largest machines in India appear to be medium size when compared internationally as the paper machines in mills abroad operate in the range of 400000- 600000 t/ annum. Most of the mills have fourdriner paper machines except newsprint which use twin wire machine. Most of the mills, established long back have multiple machines of low capacity. New mills have usually less number of machines with higher production capacity. The paper making process uses huge amount of water. However the general trend is to reuse /recycle the paper machine filtrate after clarification within the internal process. In small mills most of the mills use indigenous or second hand imported paper machines.

1.3.6 CHEMICAL RECOVERY PROCESS

Wood Based Large Mills

All the mills are well equipped with the conventional chemical recovery system to recover chemicals and energy. With increasing emphasis on reducing cost of production a number of mills are going for retrofitting / upgradation of their existing recovery plants or installation of new recovery systems to improve the efficiency. The recovery efficiency of existing systems in general is around 88 -94% as compared to 95-98% in developed countries.

Agro Based Small Mills

In view of the requirement of CREP many agro based mills have scaled up their production capacity around 100 tpd to install conventional / modified chemical recovery system. Mills below 50 tpd are going for alternate treatment option like lignin separation / recovery process for pre treatment of black liquor followed by conventional biological treatment.

1.3.7 UTILITIES

Most of the large mills are integrated mills having captive power generation. Most of them are self sustained in terms of meeting power requirement. Only a fraction of the total power requirement is purchased from grid by some mills.

1.4 EFFLUENT TREATMENT PLANT (ETP)

Various sources for generation of pollution load during the paper making process in the pulp and paper mills are given in the **Table 1.4**.

TABLE 1.4

SOURCE OF EFFLUENT GENERATION IN PULP AND PAPER MILLS

Sources	Discharge	Intensity of pollution
Fibrous raw material washing	Washing of raw materials.	Small volume with least pollutants.
Digester House	Spills & leakages of black liquor & gland cooling water	Small volume but high concentration of pollutants
Pulp washing	The final wash often referred as brown stock wash or unbleached wash	Small volume and large quantity of pollutant
Pulp bleaching	Wastewater from chlorination stage having low pH and high chlorolignins, from caustic extraction stage with dark brown colour & high pH as well as chlorolignins from hypochlorite stage	Very large volume with high concentration of pollutants. About 60-65% of wastewater is contributed from this section. The effluents contain toxic chloro-organic compounds.
Paper machine	Often referred to as white water.	Volume depending upon the extent of recycling. It contains maximum suspended solids like fibers, fines and small quantity of dissolved pollutants.
Chemical Recovery	Spills of black liquor in the evaporators, foul condensates and washings of the causticiser.	Small volumes, but high pollutants.

Effluent Treatment Plant (ETP) in Pulp and Paper Mills is meant to treat the effluent generated from the different section of the mill as given in the table 1.4. The Effluent Treatment Plant (ETP) commonly consists of the following sections-

- Screening (removal of large size suspended particles)
- Sedimentation (primary clarification)
- Biological treatment
- Secondary clarification

1.4.1 SCREENING

The effluent containing large size solids like plastics and plastic materials, small logs, papers etc. passes through the manual bar screen where these solids are removed. Some time automatic motorized bar screen are also used for removal of solids.

1.4.2 SEDIMENTATION

After screening influent enters into primary clarifier where floc's are settled down along with suspended solids impurities making fibrous sludge. This fibrous sludge is removed from the bottom of the primary clarifier through under flow pump, cake of this sludge is formed on the belt press machine. This sludge is solid to paper board manufactures.

1.4.3 BIOLOGICAL TREATMENT

In the pulp and paper industry, most of the mills have the aerobic biological system only few paper mills have anaerobic system with aerobic system.

After the primary clarifier the effluent (overflow of primary clarifier) goes to biological system where in the presence of oxygen the aerobic bacteria oxidized the most of the organic impurities. Mixed liquor suspended solids (MLSS) is developed in aeration pond by adding nutrients (Nitrogen and Phsphorous) and supplied oxygen.

1.4.4 SECONDARY CLARIFICATION

After aeration tank, all effluent with MLSS goes to secondary clarifier. Sedimentation takes place in the secondary clarifier where MLSS are settled down and then MLSS is recycled back to aerobic treatment. Some part of the treated effluent is either used in the system or released as such into the receiving stream .

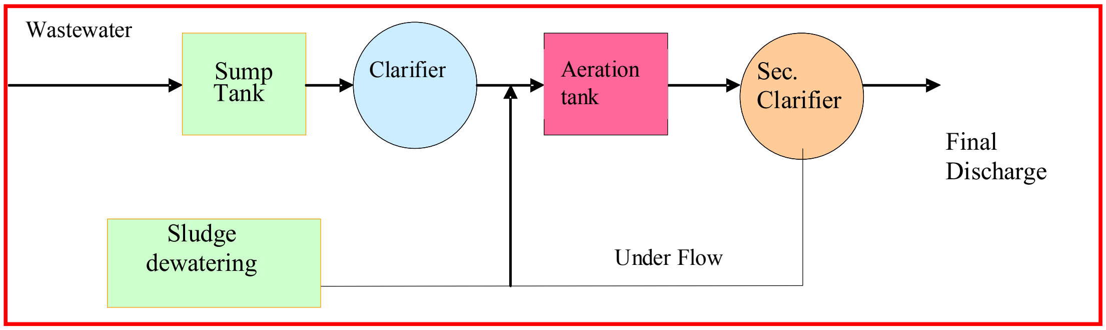

Fig 1.4 - General ETP Flow Diagram

In some cases the pulp and paper mills also incorporate a tertiary clarifier to meet the standard norms set by pollution control board for environmental compliance.

Most of the mills have the facility for treatment of their effluent which is based on either Activated Sludge Process (ASP) or combination of anaerobic treatment +ASP. In recent times there has been increasing practice of use of final treated effluent by mill or the local farmers for horticulture, gardening, irrigation of crops and plantations. Some mills have installed biomethanation system for pretreatment of black liquor followed by conventional aerobic process for treatment of pretreated black liquor along with other waste water. In RCF Based Mills the suspended matter is normally removed by Krofta (Dissolved Air Floatation system) and clarified back water is reused in pulping , pulp cleaning and washing process. Some mills are utilizing the treated effluent for land application i.e. irrigation of crops.

In the **Fig 1.5** a general block diagram of paper making process is given for better understanding.

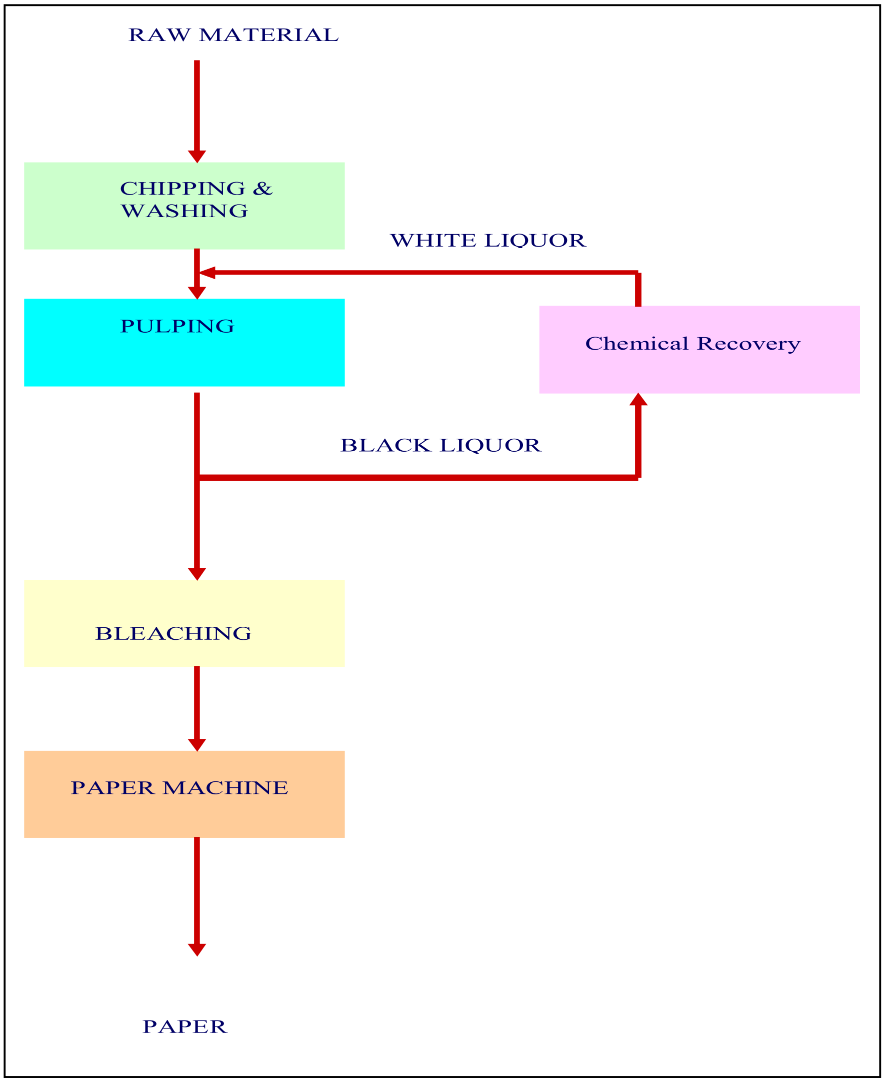

Fig 1.5 - General Flow Chart of Paper Making Process

1.5 MAJOR ISSUES BEFORE INDIAN PULP & PAPER INDUSTRIES

The various technological and environmental issues before Indian pulp and paper industries are as under

1.5.1 Technological Issues

- Use of mixed raw materials as no single raw material is available
- Low scale of operation
- Use of obsolete technology
- Use of old / obsolete equipment which were designed for processing long fiber
- High resource consumption

1.5.2 Environmental Issues

Wood Based Large Mills

- High volume of effluent.
- Discharge of chlorinated organic compounds such as AOX .
- High color in effluents.
- Solid waste management / disposal (ETP sludge, lime sludge, fly ash etc).
- Odor problem due to non-condensable gases containing mercaptans.(NCG's).

Agro Based Small Mills

- High effluent volume.
- Discharge of black liquor in absence of chemical recovery system.
- Discharge of high level of AOX and oxygen consuming substances in effluents.
- High level of pollutants & color in effluents.
- Solid waste management / disposal (ETP sludge, fly ash etc).

1.6 GENERATION OF ADSORBABLE ORGANIC HALIDES (AOX) & RELATED ISSUES

The hazardous effect of bleach effluent was considered related to use of elemental chlorine for bleaching of pulp. The major portion of lignin was usually removed in subsequent bleaching stage of pulp produced with high kappa number (35 to 40) as the conventional pulping process was having limitations to produce pulp of kappa number below 20 and secondly, because environmental issues were not given priority due to non availability of analytical method for testing of effluent for the organo chlorine compounds (AOX).

Organochlorines are a significant component of effluent from pulp mills that still use chlorine compounds for bleaching. Many organochlorines have been linked to health problems, such as cancer, birth defects, endometriosis, low sperm counts, and impaired foetal development. Organochlorines have also been shown to cause genetic damage and low survival rates of salmon and other fish. Organochlorines can last a long time in the environment (they are persistent) and build up in soils and animal, including human, tissues.

1.6.1 FORMATION OF CHLOROPHENOLIC COMPOUNDS:

The nature & extent of formation of chlorophenolic compounds are determined primarily by the residual lignin content in the pulp and type of bleaching chemicals employed. The formation of chlorinated phenolic compounds during bleaching of pulp with chlorine based chemicals are given in **Fig 1.6** which include chlorinated resin acids, fatty acids , chlorinated phenolics, dioxins & furans.

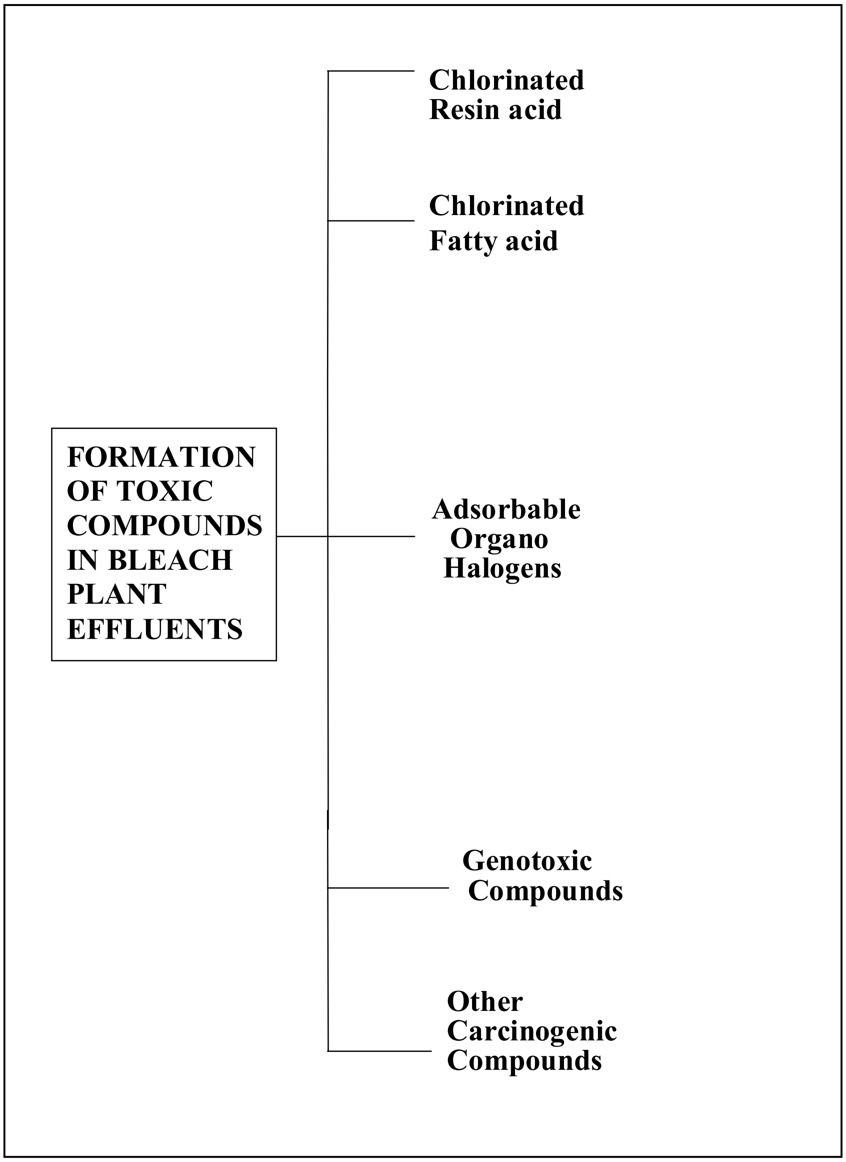

Fig 1.6 - Formation of Toxic Chlorophenolic Compounds during Bleaching

About 80% of chlorine is bound with high molecular weight lignin material (MW>1000D) commonly referred as chlorolignin. These chlorinated compounds was thought to contribute little to acute toxicity due to their inability to penetrate the bacterial cell membranes. Studies conducted revealed that these high molecular weight chlorinated phenolics are slowly decomposed in recipient water, sediments into more active biologically chlorinated catechols and guaiacols. About 20% of low molecular weight chlorinated organic material(MW<1000D) is of main environmental concern given in the fig 1.7. In recent years a considerable research efforts have been made in characterizing with respect to its individual chlorinated compounds particularly this fraction is considered to contain compounds which are toxic due to their ability to penetrate the bacterial cell membranes and has tendency to bioaccumulate in the fats of higher organism.

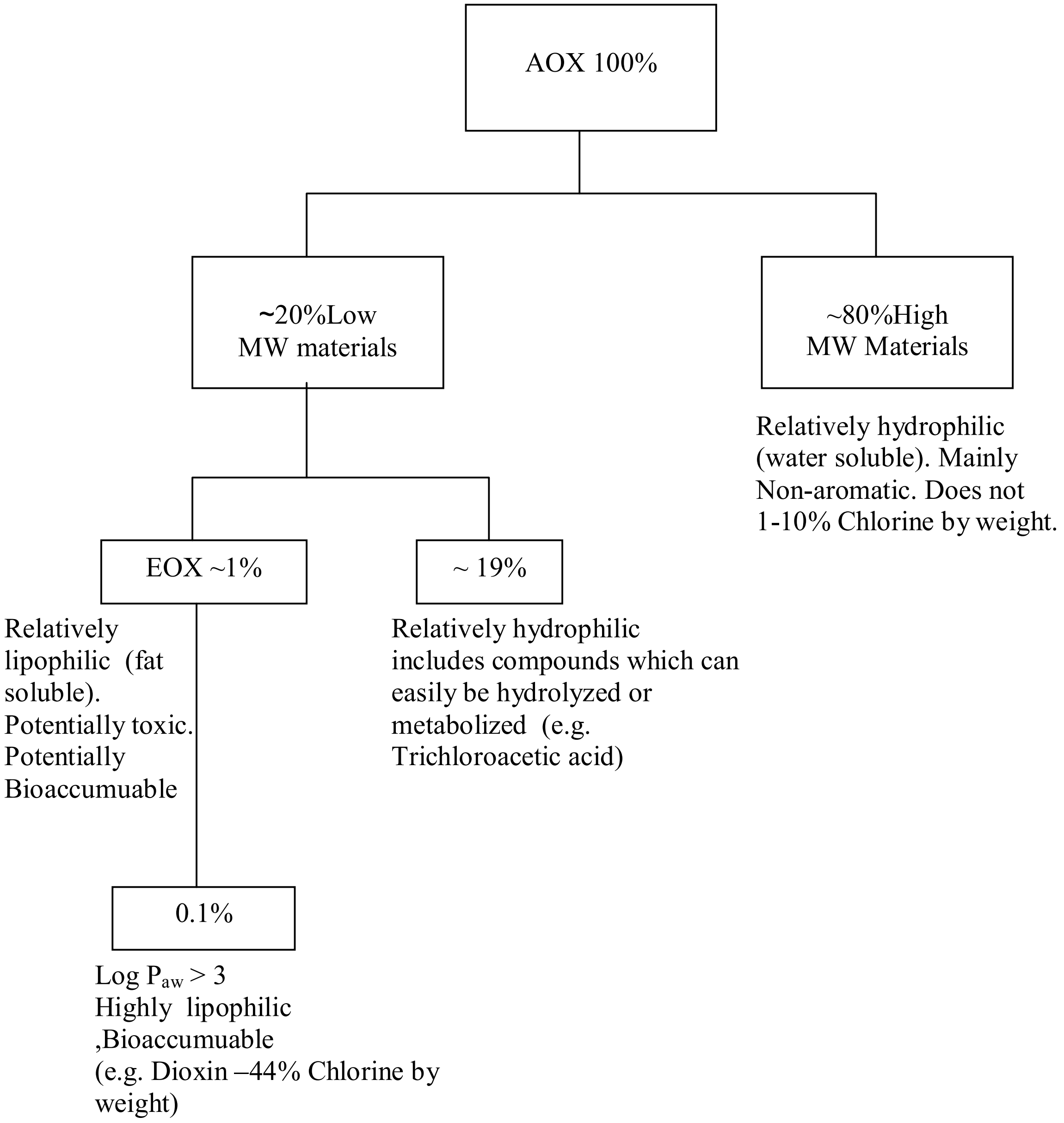

Fig 1.7 - Distribution Of Chloro Phenolic Compounds

1.6.2 IMPACT OF AOX

The consequences of toxic chloro compounds discharged in mill effluents were recognized by developed countries when high concentration of organo chlorine compounds were detected in fish fat stocks receiving bleach plant effluent. The elemental chlorine widely used for bleaching of pulp is a major contributor of organo chlorine compounds and more toxic dioxins, which has tendency for bioaccumulation, & persist in the environment. The amount of chlorinated organic compounds produced during pulp bleaching varies with raw materials, kappa number of the pulp, bleaching sequences & conditions employed.

Today with increasing environmental pressures, changing customer preferences, there is an urgent need to critically evaluate the bleaching techniques adopted by Indian paper industry. It has been well established that the discharge of chlorinated organic compounds (AOX) in the effluent and also in the end products have adverse effect on flora and fauna. The environmental hazards of bleach plant effluent are considered related to the use of chlorine containing bleach chemicals especially molecular chlorine. The developed countries recognized the consequences of toxic chemicals generated during bleaching by employing molecular chlorine and over a period of time the mills in Scandinavian countries, Canada and USA have slowly eliminated the use of molecular chlorine in last two decades and now are slowly moving towards total chlorine free bleaching (TCF) techniques.

Low molecular weight chlorinated phenolics are reported to cause acute toxicity and mutagenicity due to their ability to penetrate living cell membrane. The chlorinated organic compounds present in alkali extraction stage (E) effluent are found more toxic and contributes more than 90% of acute toxicity. The major examples of such compounds are trichlorophenol, tri & tetra chloroguaicol which have tendency to accumulate in fish and are responsible for acute toxicity. The formation of these compounds is directly proportional to the consumption of chlorine and a sharp increase in the formation of tri & tetra chloroguaiacols has been observed when active chlorine multiple was increased from 0.15 to 0.20.

Some of the chlorinated phenolic compounds like chloro catechols formed in chlorination stage have been identified as strong mutagens. Chloroform & carbon tetra chloride produced during bleaching of pulp have also been classified as carcinogenic. The use of hypochlorite in bleaching has been reported to be the major source of these compounds. Studies conducted in developed countries revealed that the fish exposed to chlorinated phenolics discharged by bleached pulp mills demonstrated impaired function of lever, enzyme system, metabolic cycle as well as increase in the incidence of spinal deformities and reduced gonad development in both laboratory and field studies.

Dioxins have received extensive attention after Stockholm declaration of dirty dozen persistent toxic pollutants (POP) where in dioxins and furans have been put under the category of unintended industrial by products as these chlorinated dioxins have not any known use.

Dioxin is a highly toxic chemical and is a probable human carcinogen. Dioxin persists in the environment and can accumulate in the tissue of fish, other wildlife and humans. It has caused cancer, liver dysfunction and toxic effects in laboratory animals.

In Indian pulp and paper industry due to use of mixed type of raw material , old technology and equipment, generate lots of toxic chemicals including Adsorbable Organic Halide (AOX) as waste product which is main concern for all the Indian paper mills. That’s why; this research is very beneficial for Indian paper mills for reduction of toxic chemicals (AOX).

1.7 OBJECTIVE OF THE STUDY

To eliminate or control the AOX in pulp and paper mills in developed countries have adopted modern fiber line technologies like ODL, ECF & TCF bleaching in which require high scale of as well as high capital investment. In Indian context , the scale of operation is low making adoption of these fiber line to reduce the AOX difficult from techno economic point of view.

In the above context this study has been taken up with following objective:

- Assessment of the level of the AOX in the bleach plant effluent generated during various bleaching sequence
- Toxicity level of the Adsorbable Organic Halides (AOX)
- Strategies for reduction of AOX
- End of Pipe Treatment studies of bleach plant effluent to reduce the level of Adsorbable Organic Halides

CHAPTER – 2.0

LITERATURE SURVEY

2.1 PAPER INDUSTRY – HISTORICAL PERSPECTIVE

The word paper is derived from the name of the reedy plant papyrus, which grows abundantly along the Nile River in Egypt. However, true paper is made of pulped cellulose fibers like wood, cotton or flax. A courtier named Ts'ai-Lun, from Lei-yang in China, was the first recorded inventor of paper circa 105 A.D. Ts'ai-Lun presented paper and a papermaking process to the Chinese Emperor and that was noted in the imperial court records. There may have been papermaking in China earlier than the above date, but inventor Ts'ai-Lun did much for the spread of papermaking technology in China. Although the history of papermaking dates back to the first century BC (Minor 1982) the modern process dates back to the opening of the Frogmore Mill in England in 1798 (Myreen 1994) producing paper from rags. The extreme short-supply of rags was alleviated in the late 1870s when it became technically feasible to produce pulp from wood. This was a turning point in the development of the industry which subsequently evolved from an artisan activity to a fully mechanised industry (Kerski 1995). Subsequently, paper mills came to be located by rivers with afforested catchments, facilitating transport of the mill wood furnish and the use of the rivers , ground water etc for power and process water. As per official records, the first Indian paper mills was started in the 1812 in Serampore (West Bengal). It was based on grasses and jute as raw material. Large scale mechanized technology of papermaking was introduced in India in early 1905. Since then the raw material for the paper industry underwent a number of changes and over a period of time, besides wood and bamboo, other non-conventional raw materials have been developed for use in the papermaking. Today paper industry in India is the 15th largest industry in the world. 2011 – 2012 year will be a land mark year for Indian paper industry, as it will be completing 200 years of its existence in India.

2.2 FIBROUS RAW MATERAL - BASIC STRUCTURE

Wood is chemically highly complex. The basic structural element of the cell walls is cellulose. Lignin and hemicellulose are also distributed throughout the cell walls, although this distribution is poorly understood (Minor 1982). The relative proportions vary, but in the cells of Scots pine, the relative proportions are 28.0 weight % lignin, 28.7 weight % hemicellulose and 40.3 weight % cellulose. In addition wood contains 3-10% of "extractives". This fraction includes fats and esters, terpenes and resin acids, phenolic materials and tannins. Trace quantities of inorganic materials are also present together with heavy metals. The lignin component binds the cellulose fibers together and in order to produce paper the fibers must be separated from each other. This may be achieved mechanically or by chemical dissolution of the lignin (Minor 1982; Fengel and Wegener 1989). The basic chemical composition of hard wood is cellulose 40-44 %, hemicellulose 25-29%, Lignin 25-31% & extractive 1-5%. The basic composition of bagasse is cellulose 26-47 %, hemicellose 19-33 %, lignin 14-23 % & ash 1-5 % on the basis of dry mass (Paturau 1989) . Other agro based residue for making paper like rice straw and wheat straw was having the basic composition cellulose 29-35 %, hemicelluloses 26-32 %, lignin 16-20 %, ash 4-9 %. (Utne & Hegbom 1992).

2.3 WATER CONSUMPTION IN PAPER INDUSTRY

Pulp & Paper Industry is a water intensive industry. Out of the total basic inputs used by pulp and paper industry water accounts for around 85 -90 %. However, it is interesting to note that out of the total water required for various operation of pulp & paper making , more than 90% is discharged as waste water implying that it is hardly consumed in the process rather it is used either as a medium of transport of pulp from one section to another or as a washing agent for removing impurities from the pulp . In last two decades though the mills have made a considerable efforts to reduce fresh water consumption but the consumption of water in Indian paper mills is still relatively high and varies from 80 -120 , 40-150 & 20-80 m^3/ton of paper in wood, agro & RCF based mills respectively (CPPRI Report)

The water consumption varies from mill to mill depending upon the fibrous raw materials used , quality of end product as well as level of technologies / equipments used for pulping and paper making process.

2.3.1 DISCHARGE NORMS OF INDIAN PAPER INDUSTRY

TABLE-2.1

EXISTING WASTE WATER DISCHARGE STANDARDS FOR LARGE PULP & PAPER MILLS

Parameters	**Standards**
Volume, m^3/t_{paper}	Writing & Printing :200 (100)* Rayon grade/ News print: 150
pH	7.0 – 8.5
BOD_3 at 27 ^{0}C mg/l	30
COD mg/l	350
SS mg/l	50
TOCl kg/t $_{paper}$	2.0

Figures in bracket are for new mills set up after 1992

(CPCB Report)

TABLE-2.2

EXISTING DISCHARGE NORMS FOR SMALL PULP & PAPER MILLS

Parameters	**Mode of Disposal**	
	Inland Surface Water	Land
Volume , m^3 / t paper • **Agro based** • **RCF based**	 200(150) 75(50)	 -
pH	5.5 -9.0	5.5 -9.0
BOD_3, mg/l at 27 ^{0}C, 3 days ,	30	100
SS mg/l	100	100
SAR	-	26

Note : Figures in ( ) indicate values for mills established after 1992

(CPCB Report)

2.4 BLEACH PLANT EFFLUENTS, CHOLOROPHENOLIC COMPOUNDS & TOXICITY

The pulp and paper industries are considered as one of most pollutant releasing industries in the world which releases different type of pollutant including AOX. (Thompson G, Swain J, Kay M, Forster C.F , 2001). D. Mohta & J.S. Upadhyaya reported that about 70 % AOX level is contributed by first two stage of bleaching sequence i.e. chlorination stage and extraction stage effluent. Bleach plant effluent from pulp mills contains chlorinated organic materials which are toxic and are also highly coloured (Bajpai, P. and

Bajpai P.K.,1994). Bergbauer, M. and Claudia Eggert, C., (1992) reported that bleaching of pulp fiber is done by chlorine as bleaching agent in chlorination stage and subsequently extraction stage which contribute most of the pollution load as AOX . Milosevich, G.M. & Hill, D.A., (1992), studied and shows that bleach plant effluent carry high value of AOX than the other stream. Wagner, J. (1981) also studied & reported that water pollution problem and toxicity in the pulp and paper industries originate largely from Bleach Plant Effluent.

The principal aim of pulp bleaching is to increase the brightness of the pulp. Organically-bound chlorine, arising from the chlorination of lignin and extractives, is found in significant concentrations in bleached kraft pulp effluent (Reeve, D.W., 1991). The effluent discharge from bleaching section contains large amounts of chlorinated organics & can be problematic in the environment, and the paper industry would prefer they should not be discharged prior their characterization & treatment (Prasad, D.Y., & Joyce, T.W., 1993).The insufficient washing of unbleached pulp leads to increased dioxins and furans after chlorination stage of softwoods (Hise, R.G., et.al, 1990). The chromophoric (light absorbing) components in pulps are predominantly functional groups of degraded and altered residual lignin which is both darker and more tightly bound to the fibers than the original lignin component. This can either be converted and stabilised (lignin preserving bleaching) or removed (lignin removing bleaching) (McDonough 1992). The chemical stability of organochlorine compounds in bleach effluents is reflected in their resistance to microbial degradation, and this fact coupled to their ubiquitous occurrence in environmental samples has aroused widespread concern (Nielson, A.H., Allard, A.-S., Hynning, P.-A. & Remberger, M., 1991)). Gonzales, P., Zaroor, C., (2000) reported that softwood pulp contains high amount of resin & fatty acid & require high bleaching chemicals during conventional bleaching sequence as compared to hard wood pulp and resultant in high amount of AOX released in the effluent.

Pulp & paper mill effluents originated in cellulose pulp manufacturing process are usually toxic, specially the bleaching effluents, which exhibit high contents of halogenated organic compounds. (Ali & Sreekrishnan 2001). Hormonal changes in fish and their communities were demonstrated, which could be attributed to endocrine-disrupting chemicals (EDCs) contained in bleached effluents. This chronic toxicity is attributable to extractive compounds, such as resin acids, sterols, and fatty acids present in the bleached mill effluents (Vidal, G., et.al 2007).

Effluents from pulp and paper bleach plants using chlorine to be extraordinarily complex. Suntio et al. 1988 published a compilation of over 250 chemicals present in pulp mill effluents. 180 of those listed are chlorinated compounds comprising phenolic, together with neutral and acidic compounds. The chlorophenolic compounds, particularly chlorophenols, catechols, guaiacols and syringols are important components and have, for example, been isolated from samples taken in every sub-basin of the Baltic Sea (Sodergren 1993). A proportion of these compounds appear to be derived from the degradation of high molecular weight chlorinated material formed during chlorine bleaching (Martin et al. 1995). It is only recently that reference compounds for some of these exotic chemicals have been synthesised for analytical purposes (Smith et al. 1994 a & b; Hyotylainen 1994).

Elemental chlorine reacts primarily with residual lignin to produce approximately 4kg of organically bound chlorine per tonne of pulp produced, although this figure will vary according to the kappa number of the pulp being bleached and the specific bleach sequence. Various types of reaction mechanism can be involved and the diversity of such reactions is usefully described by Bergman et al. (1994). About 70% of the organically bound chlorine is present as high molecular mass material in spent liquor from the bleach. In the extraction liquor about 95% is bound as high molecular mass compounds with high carbon to chlorine ratios. Although these are thought, in themselves, to be biologically and toxicologically inactive, no data exist concerning the activity and fate of their degradation products. In addition, their high relative molecular mass coupled with their polarity renders them difficult to analyse by established chromatographic techniques (Kringstadt & Lindstrom 1984).

The toxicity of the effluents were also tested according to the standardized luminescence bacteria test procedure (DIN 38412 Teil 34 1991) by ToxAlert 10 instrument. Comparison of Microtox Toxicity with other toxicity tests has pointed out the satisfactory sensitivity of microtox for analyzing the toxicity of pulp and paper mill effluents (Juha Fiskari and Pertti K. Hynninen 2000). Gergov, M., Kangas, A. & Kukkonen, K., (1988) also reported that toxicity of Extraction stage filtrate was rather high as compared to other stage effluent and it was even higher during bleaching with a higher chlorine dioxide concentration.Bleached kraft pulp mills effluent were studied for Toxicity reduction evaluation to identify the sources of, and identify a method for reducing , their effluent chronic toxicity to marine organisms (Hickman, G.T. & Miller, J.P., (1993). Untreated and secondary treated conventional (Cl2) bleaching, total chlorine free & elemental chlorine free bleqaching effluents were assessed by different biological toxicity test (Ahtiainen, J., Nakari T., & Silvonen, J. 1996).

2.5 DETERMINATION OF AOX COMPOUNDS & THEIR CHARACTERISATION

Several hundred individual chlorinated organic compounds – Phenolic acid, ketones, lactose and aldehydes, dioxins and furans have been identified in bleach plant effluent. In addition large fraction of the organically bound chlorine in the effluent is attached to high molecular weight material. But Identification & quantification of individual chloroorganic compounds was exceedingly complex and so generic measurement was desirable whereby the total amount of chlorine bound to organic matter is quantitively determined (Odendahl, S.M., Weishar, K.M. & Reeve, D.W., 1990). The AOX measurement in the soil and water have shown that the halogenated compounds are more widespread than previously assumed and that there is substantial natural production of organo halogen in natural environment (Olof

Dahlman, et al. 1993). The high molecular weight material may be relatively benign. It is too large to penetrate living cells, highly water soluble and so will not bioaccumulate. Some of the low molecular weight compounds are known to be toxic and persistent to bioaccumulate and have been associated with various sub lethal effects. As a result discharge of chlorinated organic matter was regulated in Sweden, Germany, France and several provinces in Canada (Douglas W. Reeve, 1991). There are some analytical methods for measuring a "sum parameter" approximating the total amount of organically bound chlorine. The principal of all methods are same as separation of the organically bound chlorine from inorganic chlorine i.e. chloride ion, mineralization of the organically bound chlorine, determination of the chlorine ion produced on mineralization. In Sweden, a relatively complex method known as TOCl (Total Organic chorine) has been used to establish much of the back ground data and was considered the basis for Swedish regulation. Public fears about AOX in kraft pulp mill effluent started in the early 1980s in association with previous fears about dioxins which is small part of AOX compounds and culminated with several provincial governments setting stringent parameter limits in the late 1980s (Lindsay and Smith 1995). Bruce I. Fleming (1995) has studied and said that distinguish between toxic and harmless organochlorines, just as we distinguish between poisonous and edible mushrooms so regulatory body can make norms for discharge of persistent , toxic & bioaccumulating substances, no matter what elements they contain.

As a result of the complexity of bleachery effluents in relation to their organochlorine content, there has been a trend towards monitoring their discharge by means of the group parameter AOX. AOX (Adsorbable Organic Halogens) measures the quantity of organically bound chlorine present in a sample (Neilson et al. 1991). In order to evaluate the environmental impact of effluents from the production of bleached kraft pulps according to pulping bleaching technology applied in Swedish mills, comprehensive chemical and biological characterization studies have been carried out (Stromberg, L. et al. 1996).

The preferred method, which is more widely used, is known as AOX (Adsorbable Organic Halide) (J.L.Fraser and D.W.Reeve 1992). The amount of AOX formed is linearly proportional to the total consumption of elemental chlorine in Cl2 & ClO2 (P. Axegard 1989).

AOX is primarily non-toxic material (99%) with a small amount of fat-soluble toxic chlorinated organics (1%). While AOX is not a measure of toxicity, the associated fat-soluble chlorinated group (dioxins, furans, & polychlorinated phenolic compounds) is considered to be toxic with bio-accumulative tendencies. The chloroorganic compounds collectively known as AOX formed during bleaching of the pulp with chlorine based chemicals is known to cause toxicity of aquatic life and tendency to bioaccumulate (Fraser, J.L. & Reeve, D.W., 1992). Since 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) has been found to cause cancer in rats, it is considered the most toxic of the dioxin group and governments have focused primarily on controlling TCDD (Harrison and Hoberg 1994). The majority of organochloride present in the pulp and paper mill effluents are high molecular weight cholrolignins i.e. more than 1000 Da. These compounds are likely non biodegradable and have small contribution to the toxicity (Ali & Shreekrishnan 2001). On the other hand low molecular weight chlorinated compounds are major contributors to mutagenecity and bioaccumulation due to their hydrophobicity (Savant et al. 2006). Organochlorines are a group of chemicals including dioxins and furans, at least some of which are highly toxic to humans. Organochlorines are formed as a byproduct of the chlorine bleaching process in pulp mills (Hocking, J., 1991). Chloro organic compounds become bound to natural matrices - particularly sediments - but there are inherent problems on the bioavailability of the compounds. (Nelson A.H., et al. 1990)

In 1976, an Italian industrial accident released a cloud of toxic gases containing 2,3,7,8-TCDD (Fortunati 1984). This accident greatly contributed to dioxin awareness throughout the world. Researchers identified dioxin to be the most potent carcinogen tested to date in rats (Kociba and Keyes 1978). Shortly after the Italian accident in Britain, the cover-up of a 1968 dioxin trichlorophenol chemicals plant accident, exposing 70 workers to dioxin, began to leak to the public. A journalist covering the story called dioxin "the most deadly poison known to man" (Cox et al. 1986).

In Canada in the late 1970s, dioxin was found in fish and herring gull eggs around the Great Lakes (Norstrom and Simon 1983; Hallett 1984). Dioxin was measured in human adipose tissue in people living east of the Great Lakes (Boddington et al. 1983). In Canadian pulp and paper Industry a senior manager was legally charged for failing to meet the effluent toxicity regulation (Riebel, P.N, et al., 1997).

Dioxin was measured in human adipose tissue in people living east of the Great Lakes (Boddington et al. 1983). In the mid-1980s, whale kills were associated with dioxins (Boddington 1984). Dioxin was found in chicken livers from flocks housed on wood shavings previously treated with pentachlorophenol (Boddington et al. 1983). Discussions on dioxin/furans in Canada were formulated under the National Research Council of Canada, investigating both the analytical developments and environmental/human health effects (NRCC 1981). Increased interest by various agencies and the public can be attributed to confusion with 2,4-D herbicide issue (Maybury et al. 1982),

Pulp Mill waste water continues to wreak havoc on surrounding ecosystems. In laboratory tests, mill effluent causes reproductive impairment in zooplankton, invertebrates (both these are food for fish), and shellfish, and genetic damage and immune system reactions in fish (Easton et al. 1997)

Murray W. D.& Mark Richardson, (1993) reported that the pulp and paper industry produces large quantities of organic and chlorinated organic wastes and AOX compounds that are toxic and/or mutagenic, difficult to degrade, and have a propensity to bioaccumulate pose a serious human health hazard. Gordon, R.C., et.al. (1990**)** also reported that some AOX compounds were lipophilic and can penetrate cell membranes and tend to bioaccumulate.

In 1986, the U.S. EPA and pulp and paper industry agreed to conduct a joint screening of a small groups of mills (The 5 Mill Study) aimed at determining the source of dioxin/furans and quantifying untreated/treated wastewater effluent and sludge concentrations (Amendola 1989).

A Swedish study reporting furans in milk cartons surprised the pulp and paper industry, and initiated extensive studies in several countries (Ryan et al. 1988). A second NCASI investigation of all U.S. mills (The 104 Mill Study) using chlorine-bleaching processes found dioxins/furans (Whittemore et al. 1990). Other U.S. investigations into milk cartons and other food packages determined that dioxins/furans contamination levels depended upon food fat content, storage temperature, contact time, and container barrier coating (LaFleur et al. 1990). The Ontario Ministry of Environment reported 2,3,7,8-TCDD in 17 of 47 samples of fish downstream of kraft operations in levels greater than the Ontario consumption guideline of 20 parts per trillion and dioxin/furans were in sludge from nine bleached Kraft pulp mills (Clement et al. 1989). Fish exposed to chlorinated phenolics discharged by bleached pulp mill are reported to have demonstrated impaired function of liver, enzyme system, metabolic cycle as well as increase in the incidence of spinal deformities and reduced gonad development in both laboratories and field studies (Larsson, L., T. Andersson, L. Forlin and J. Hardig ,1988).

Bioaccumulation of the chlorinated dioxins and dibenzofurans in commercially important aquatic species led to the closure of several fisheries in Canada in late 1988 (Hocking 1991). The potential importance of local discharges upon fisheries and fish consumers may be assessed from the work of Svensson et al. (1991). The scale of the problems encountered is reported by Whittle et al.(1993). A case specific US study is described by Schell et al. (1993) while bioaccumulation of dioxins in a Canadian river system is described by Owens et al. (1994).

2.6 MEASURE TO REDUCE THE CHLORO PHENOLIC COMPOUNDS

In 1992, British Columbia government enacted the Pulp & Paper Mill Liquid Effluent Control Regulations, setting strict AOX limits over a series of stages to eliminate chlorinated organic compounds within 10 years. Pulp mills had to reduce their actual AOX discharge limit and could follow one of two approaches to eliminate AOX before 2003, ensuring the elimination of chlorine and chlorine dioxide bleaching processes. The industrial waste branch of B.C.'s Ministry of Environment, Lands and Parks claimed that the new regulation represented a "precautionary" approach to the pulp mill effluent problem, since only about 10% of pulp mill effluent 30,000 different products had been identified (Van Nijnatten et al. 1997).

Chemical precipitation of chlorinated organic material by iron and or aluminum salts has been reported as a potential AOX removal system (Wilson, D.G. & Holloran, M.F., 1992).

Adsorabable organic halides (AOX) can be efficiently reduced by adsorption, ozonation and membrane filtration techniques **(**D. Pokhrel, T. Viraraghavan, 2004**).**

Milosevich, G.M. & Hill, D.A., (1992) studied the treatment of bleach plant effluent with lime mud shows that neutralization of bleach plant with lime mud, followed by the addition of alkaline sulphide process liquor was demonstrated to be a practical, cost-effective method of reducing mill AOX discharge. Organic matter from spent bleaching effluents (from chlorination (C) or extraction (E) stages, or a mixture of both) was effectively precipitated chemically and AOX in E- stage effluent is reduced upto73% (Milestein, O. 1988). D.W. Francis (1998) also reported that the AOX reduction by combined chemical and biological treatment ranged from 53 to 59% depending on the operating conditions of the biological treatment plant.

Standard practice for end of pipe (EoP) waste water treatment is biotreatment (Activated Sludge Process , Aerated Stabilisation basin/ Aerated Lagoon, Anaerobic process) which reduce AOX from 8 – 60% (Gary Hickman, 1995). The activated sludge treatment process has become widely adopted due to its optimization in relation to AOX removal. 40–60% reduction in AOX was observed during effluent treatment process (Gergov et al., 1988, Jussila, 1989). But the AOX reduction achieved in an aerated lagoon are lower at around 20 – 40% (Kurten 1989, Kalliola 1988, Simpura 1989). The anaerobic process has not been tested on the mill scale with the total waste water containing bleach plant effluent because anaerobic bacteria is very sensitive to the bleach chemical (R.Saunamaki, K.Jokinen, R.Jarvinen & M.Savolanien, 1991. The use of micro fungi in waste water treatment is being studied intensively. Tests have already achieved an AOX reduction of around 70% but this method is still at the laboratory stage (Matsumoto et al. 1987, Zuner 1987, Ek & Erikson 1987, Hattakka 1988).

Sierka R.A. & Bryant, C.W. (1994) studied that changes in kraft bioeffluent quality were evaluated as a function of increased chlorine dioxide (ClO2) substitution, and ultrafiltration (UF) membrane and heterogeneous photocatalysis (HP) treatment of extraction (E-stage) wastewater prior to aerobic biological treatment.

Fergusan J.F. attempted AOX removal by combining anaerobic treatment and aerobic treatment and found that the AOX reduction were 30-35 % with anaerobic treatment and 40-45 % with aerobic treatment. And combination of anaerobic and aerobic treatment resulted in to 50-55% reduction in the AOX level.

More attention has been paid to aerobic cultures specially white rot fungi. 40 - 60% AOX reduction was shown by Phaenerochaete chrysosporium from bleach pulp effluent (Chang HM , Joyee TW et al.)

Treatment of kraft bleach effluent with mixture of thermophilc aerobic and anaerobic culture reduces 36-56 % AOX (Rintala et al.)

The theory of chemical reactions in for the treatment of effluent is very complex . The chemical reactions are often incomplete , and numerous side reactions with other substances in wastewater may take place. (Metcaff & Eddy)

The secondary effluent treatment in aerated lagoons or activated sludge plants is an important and technologically well tried technique for reducing the load of organically material in the mill effluent before discharging it to the recipient. Although initially designed for BOD reduction it is now recognized that biological treatment plants also are effective for controlling discharges of organic & inorganic matter measured as AOX, COD or specific compounds. These biological process are generally also effective in reducing the acute toxicity of kraft mill effluents (Lars Stromberg et al. , book, 1996)

The Secondary waste water treatment plant of bleached kraft pulp mills were opted to remove 90 – 97 % BOD but the concomitant removal of organic halogen (AOX) was only 30 – 60 % depending on the mill & method treatment (Saski et al , Book) . Measurement made at mill scale biological treatment confirm that a full fladged with good operated plant can reduce AOX about 50% (Saunamaki, R. et al., 1991)

More over the most of the studies have been related to ECF & TCF effluents which are less toxic and easy to handle as compared to conventional method where use of elemental chlorine has thus promoted the closed water cycle concept in these mills. The introduction of elemental chlorine free (ECF) bleaching process and oxygen delignification substantially reduced bleaching chemicals use, effectively eliminated AOX levels and achieved significance decreases in recalcitrant compounds from bleach effluents (Chaparro, T.R. et al 2010)

Traditionally, the internationally kraft pulp & paper industry has used aerobic biological system, for external treatment of their waste waters. In many cases , aerobic lagoons have been installed , because of their ease of operation and good tolerance against shock loads and varying condition. The activated sludge treatment also has wide spread application and in Finish pulp and paper mills a number of plant have been installed (B. Frostell 1994). However there is no reference of application of such technologies for treatment of bleach effluents from conventional chlorine based bleaching sequences as used in Indian mills. Therefore the present project studies will be directed towards evaluation of potential of some of these technologies in reducing the pollution load and toxicity of bleach plant effluents generated in Indian mills. The inhibition of light production of Vibrio fisheri luminescent bacteria indicates disturbance of the energy metabolism of this heterotrphic bacterium. Because this luminescent pathway is direct branch of electron transport chain the luminescent measurement assesses the metabolic status of this bacterium. Hence the change in bacterial luminescence when these bacteria are exposed to wastewater samples can be used as an indicator of potential toxicity (J.Ahtianien et al.). The sensitivity of the microtox method has been proven to be comparable to acute toxicity tests with fish and crustaceans in several comparative investigations (B.Eklund et al.)

2.7 TECHNOLOGICAL DEVELOPMENT FOR REDUCTION IN AOX

Pulping and bleaching are the thrust areas where remarkable technological developments have taken place in the last two decades in the developed countries to reduce the overall environmental impact (including AOX) associated with pulp and paper industry. Due to the relatively poor degradability of AOX compounds, the attainment of the anticipated effluent regulation will not be possible without the aforementioned in plant bleachery modification (Cook, 1990). In recent years the trend in technology developments or approach for reducing AOX have been have been :

- Extended delignification (Modified batch pulping process)
- Improved pulp washing
- Oxygen delignification

- Development of Elemental chlorine free (ECF) and Total Chlorine free (TCF) bleaching techniques.

2.7.1 MODIFIED PULPING

The extended delignification process includes modified cooking like RDH and super batch cooking. The main objectives of these techniques is to reduce the kappa factor (residual lignin in pulp)to the lowest possible level in cooking stage itself, since the conventional pulping process has limitations to cook certain fibrous raw material to low kappa number. High kappa number of unbleached pulp demands more bleaching chemicals and ultimately increase the pollution loads in the mill effluent. These modified batch cooking and continuous cooking processes are highly energy efficient and produce pulp of low kappa number with improved pulp viscosity.

The other advantages of these processes besides reduction in AOX level are as under:

- Reduced energy consumption by 60-70%
- Reduction of chemical consumption in pulping and bleaching.
- Lower kappa number of pulp.
- Higher pulp yield with reduced fiber loss.
- Improvement in pulp quality leading to improvement in paper machine
- runnability.
- Reduced alkali losses.
- Low viscosity of black liquor as a result firing can be done at 75-80% solids.
- Less emission of obnoxious gases like Mercaptans
- Reduced TRS emission. kg /t paper

2.7.2 IMPROVED PULP WASHING

The washing of pulp serves to separate pulp fibers from spent pulping liquor which contains both inorganic cooking chemicals and the organic substances dissolved from fibrous raw materials. Brown stock washers are generally used by the mills for washing of pulps. The efficiency of the washing equipment generally depends upon nature of fiber and equipment used.

Washing of pulp has significant role in influencing not only the process economy through recovery of chemicals used in cooking of raw materials and reduced bleaching costs but also minimize the carryover of organic substances along with pulp to bleaching section and ultimately reduce the environmental impact associated with the discharge of toxic chlorinated phenolic compounds. AOX value in bleach plant effluent is also depend upon the COD carry over with pulp going to bleaching section. In Indian condition COD carry over is high resultant in to high AOX value. At certain COD carry over, AOX discharge from softwood pulp bleaching were clearly higher than the hard wood pulp bleaching.(Bloomberg, L. 1990).

In view of improving the washing process, new generation of pulp washing equipments have been introduced in last decade which have minimized washing losses and carryover of organic substances along with pulp to bleach plant. Some of the examples ;

- Drum displacer washer
- Screw press in combination with rotary drum washers.

Screening operation is also considered an integral part of pulp washing where knots, shives and other impurities are removed. Thus dewatering after screening has the function of final washing stage, when its filtrate is used as wash liquor in previous stages (counter current washing). This is known as “Closed Screening” where specially designed equipment is provided to avoid the risk of foaming due to increased concentration of dissolved salt and organic substances in circulating liquor. The closed screening system is now a common practice employed by the mills in developed countries to reduce pollution.

2.7.3 OXYGEN DELIGNIFICATION PROCESS

The oxygen delignification which is often termed as extended delignification is a well established technology & almost all mills in developed countries have adopted oxygen delignification to reduce kappa number of pulp prior to bleaching. The process reduces the kappa number by 40-50%, chlorine consumption by 50-60% and AOX generation by 60-70%. Some of the mills in developed countries have even adopted two stage oxygen delignification to reduce the kappa number to lowest possible and the spent liquor from oxygen stage is taken to chemical recovery along with black liquor. The efforts are continued to reduce kappa number further below 10 in order to improve the process efficiency and environmental compatibility.

2.7.4 MODIFIED BLEACHING PROCESS

The bleaching process serves the purpose to extract out the residual lignin and increase the brightness of the pulp used for the manufacture of different grades of bleached variety of paper products. The elemental chlorine is generally used to increase the solubility of the residual lignin from pulp and hypochlorite is used for brightening the pulp. The release of various chlorinated phenolic compounds including toxic dioxins during bleaching of pulp with chlorine based chemicals particularly elemental chlorine had forced the industry to adopt new elemental chlorine free (ECF) and total chlorine free (TCF) bleaching techniques. Considerable R&D efforts have been put in the development of these techniques.

Thus most of pulp mills abroad have switched over to the elemental chlorine (Cl2) free bleaching (ECF) technology using chlorine dioxide bleaching looking into its advantages in significant reduction in formation of dioxins, furans and AOX related compounds along with improved brightness attainment. Recently ozone has attracted the attention of the paper industry as one of the most effective bleaching agents and some of the mills have adopted the total chlorine free bleaching (TCF) techniques using ozone, oxygen and hydrogen peroxide. The adoption of TCF bleaching has led to the concept of system closure as no toxic chlorinated compounds and recalcitrant are present in TCF effluent. The modern bleaching sequences used by the industry are given as under :

TABLE-2.3

MODERN ECF & TCF BLEACHING SEQUENCE

ECF	OD (EOP) D (PO),OQ (OP) (De)D,OQZ(EO)D
TCF	OQ (EOP) Q (PO),OQ (PO) PP,OQZQPO
O= oxygen, D= Chlorine dioxide, De= Chlorine dioxide with alkalinity added, P= Peroxide Q= Complexing agent, Z= Ozone	

The pulping and bleaching process employed in Indian pulp and paper mills and in developed countries are as under :

TABLE-2.4

PULPING AND BLEACHING EMPLOYED IN INDIAN AND IN DEVELOPED COUNTRIES MILS

Particulars	Indian Paper Mills	Paper Mills In Developed Countries
Raw materials	Mixed	Wood based
Pulping process	Usually conventional	Modified
Pulp washing, carry over kg COD/t of pulp	>20	<10
Oxygen Delignification	No	Yes
Kappa No.	18-26	10-12
Bleaching practice	Conventional	ECF &TCF

The application of the new modified pulping and bleaching technologies have been limited mostly to the developed countries primarily due to consistent supply of fibrous raw materials of uniform quality & high scale of operation of the mill. In India, the major bottlenecks in adoption of these technologies have been low scale of operation and use of mixed fibrous raw material. The scale of operation in the mills in developed countries varies between 1000-2000 t/day whereas in Indian mills it lies between 30-850 tpd .

Similarly in case of ECF bleaching technologies one of the main requirement for induction of chlorine dioxide stage is the complete changeover from MS to special grades of alloyed stainless steel (SS) system to prevent corrosion. This calls for heavy investments and scrapping the entire system in bleaching section for chlorine dioxide. In recent times the large mills have started partial replacement of chlorine by chlorine dioxide. A few mills have switched over to ECF bleaching

The adoption of these new technologies involves huge capital investment (around Rs. 80-90 crore) as most of these process and equipments are of imported origin. Due to the increased environmental awareness, stringent discharge norms, competitive market the industry is exploring the possibilities of adopting these new technologies for their sustenance in the competitive globalised scenario. However, the elemental chlorine and hypochlorite are still the dominating bleaching chemicals used in Indian mills (CPPRI Project Reports).

CHAPTER - 3

CHARACTERIZATION OF BLEACH PLANT EFFLUENTS

The chapter includes the detailed characterization of bleach plant effluents collected from large wood based mill and small agro based mill for various pollution parameter including AOX.

3.1 COLLECTION AND PRESERVATION OF EFFLUENT SAMPLES

3.1.1 COLLECTION OF SAMPLES:

The effluent sample were collected through composite sampling (24 hours) at selected mills. To ensure sample integrity, samples were properly labeled with date, time and place of collection.

3.1.2 PRESERVATION OF SAMPLES

Sample collected were preserved as per APHA method to minimize chemical & biological changes that inevitably occur during transportation of collected sample from mill site to laboratory.

PRESERVATION TECHNIQUES:

Preservation of samples for determination of various pollutional parameters was carried out as per **Table – 3.1.**

TABLE – 3.1

PRESERVATION OF SAMPLES FOR DIFFERENT ANALYSIS

Parameters	**Container Type**	**Sample Size In ml**	**Preservation Technique**	**Maximum Storage Period Recommended**
BOD	P,G	1000	Refrigerate	06 h
COD	P,G	100	Analyze as soon as possible or add H_2SO_4 to pH <2; Refrigerate	07 days
Color	P,G	500	Refrigerate	48 h
Oxygen (Dissolved)	G, BOD Bottle	300	Analyze immediately Titration may be delayed after acidification	0.5 h.
pH	P,G	-	Analyze immediately	02 h.
Solids	P,G	-	Refrigerate	07 days

P = Plastic, G = Glass

Source: APHA Book

3.1.3 PROCEDURE FOR PRESERVATION OF SAMPLE FOR AOX

- The composite effluent samples were collected and analysed for free residual chlorine if any.
- To reduce the free chlorine a little quantity of sodium sulfite was added.
- The effluent sample was then acidified with Concentrated nitric acid (AR grade) to about pH ~ 2.

- The acidified samples were preserved in good quality plastic bottles (200 ml) ensuring no air bubble present in head space of bottle.
- Sample bottle were then brought in an icebox to the testing laboratory.

3.2 ANALYSIS PROCEDURE

Pollutional parameter like pH, SS, COD BOD, etc were determined as per "Standard methods for the Examination of Water and Wastewater" prepared and published by American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollutional Control Federation (WPCF). While AOX was determined as per DIN 38409 Tail 14 AOX procedure.

The procedure followed for analysis is given below:

3.2.1 DETERMINATION OF pH

This method describes the procedure for determination of pH of black liquor to indicate presence of either acidic or basic ions which contribute towards physicochemical properties of black liquor.

MATERIALS:

I) APPARATUS:

- Any commercial pH meter including a glass electrode and calomel reference electrode. The meter must be capable of indicating pH to ±0.1 unit or less.
- Beakers, 50 ml & 100 ml capacity.
- Magnetic stirrer.

II) REAGENTS:

- Potassium hydrogen phosphate buffer (pH 4.01 at 25˚C) – Dissolve 10.21 gram of potassium hydrogen phosphate in water & dilute to 1000 ml.

- Borax buffer (pH 9.18 at 25˚C) – Dissolve 3.18 gram of $Na_2B_4O_7.10H_2O$ in carbon dioxide free water and dilute to 1000 ml. The $Na_2B_4O_7$ need not be dried before use, but should be kept tightly sealed to prevent moisture or CO_2 uptake before use.

III) METHOD

CALIBRATION OF EQUIPMENT

Before measuring the pH of the black liquor, calibrate the pH meter using phosphate buffer for pH 4.01 and borax buffer pH 9.18 at 25˚C. Follow the manufacture's instructions for calibration of the procedures in ASIM D1293, Standard Test Method for pH of water or ASIM E70, Standard Test Method for pH of aqueous solutions with the glass electrode. The potassium hydrogen phthalate buffer and borax and borax buffers are usually used for calibration when sample shows an unusually high or low pH.

PROCEDURE:

Place 50 ml of black liquor in a 100 ml beaker. The beaker is placed on a magnetic stirrer and the electrode is dipped in sample with a magnet. The sample is stirred till constant pH.

REPORT:

Report pH readings as the average of two determinations to the nearest 0.1 pH unit.

3.2.2 DETERMINATION OF TOTAL SUSPENDED SOLIDS

Analysis of suspended solids is important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agencies standards. A well-mixed sample is filtered through a weighed standard glass-fiber and the residue retained on the filter is dried to a constant weight at 103 to 105ºC. The increase in weight of the filter represents the total suspended solids.

MATERIALS

(I) APPARATUS

- Glass-fiber filters without organic binder.
- One of the following, suitable for filter disk selected:
    - Membrane filter funnel.
    - Gooch crucible, 25ml to 40ml capacity, with Gooch crucible adapter.
    - Filtration apparatus with reservoir and coarse (40-60μm) fritted disk as filter support.

- Suction flask, of sufficient capacity for sample size selected.
- Desiccator, provided with a desiccant containing a color indicator of moisture concentration.
- Drying oven, for operation at 103 to 105 ºC.
- Analytical balance, capable of weighing to 0.1 mg.

METHOD

Procedure: Dry the glass-fiber filter in an oven at 103-105 ºC temperature for an hour, cool in desiccator and weigh. Assemble filtering apparatus and filter. Wet filter with a small volume of distilled water to seal it. Filter measured volume of well mixed sample through glass fiber filter, wash with three successive 10 ml volumes of distilled water, allowing complete drainage between washings & continue suction for about three minute after filtration is complete. Carefully remove filter from filtration apparatus and dry for at least 1 hour at 103 to 105 ºC in an oven. Cool the filter in a desiccator to balance temperature and weigh. Repeat the cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until the weight loss is less than 4% of the previous weight or 0.5 mg whichever is less.

Calculation:

$$\text{Total suspended solids, mg/l} = \frac{(A-B) * 1000}{\text{Sample volume, ml}}$$

Where,

A = Weight of filter + dried residue, mg.

B = Weight of filter, mg.

3.2.3 DETERMINATION OF TOTAL DISSOLVED SOLIDS

A well mixed sample is filtered through a standard glass fiber filter and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180ºC. The increase in dish weight represents the total dissolved solids.

MATERIALS:

I) APPARATUS:

- Glass fiber filter disks
- Filtration apparatus
- Membrane filter funnel
- Filtration apparatus with reservoir and coarse (40 to 60 µm) fritted disk as filter support.
- Suction flask
- Evaporating dishes.
- Desiccator.
- Steam bath.
- Drying oven, for operation at 180±2ºC.
- Analytical balance, capable of weighing to 0.1 mg.

METHOD:

PROCEDURE:

Filter measured volume of well mixed sample through glass fiber filter. Transfer known volume of filtrate to evaporating dish and evaporate to dryness on a steam bath. Dry for at least one hour in an oven at 180±2ºC. Cool in desiccator to balance temperature and weigh. Repeat the cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until the weight loss is less than 4% of the previous weight or 0.5 mg whichever is less.

Note: As excessive residues in the dish may form a water trapping crust, limit sample to not more than 200 mg residue.

Calculation:

$$\text{Total dissolved solids, mg/l} = \frac{(A-B) * 1000}{\text{Sample volume, ml}}$$

Where,
A = Weight of dried residue + dish, mg.
B = Weight of dish, mg.

3.2.4 DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD)

Principle:

Biochemical Oxygen Demand is the measure of degradable organic material present in a water sample and can be defined as the amount of oxygen required by the micro-organisms in stabilising the biologically degradable organic matter under aerobic conditions.

Apparatus:

i. BOD bottles
ii. BOD incubator

Reagents:

i. Phosphate buffer:

Dissolve 8.5 gram KH_2PO_4, 21.75 gram K_2HPO_4, 33.4 gram Na_2HPO_4, $7H_2O$ and 1.7 gram NH_4Cl in distilled water and dilute to one liter. pH should be 7.2.

ii. **Magnesium sulphate solution:**

Dissolve 22.5 gram $MgSO_4$ $7H_2O$ in distilled water and dilute to one liter.

iii. **Calcium chloride solution:**

Dissolve 27.5 gram of $CaCl_2$, in distilled water and dilute to one liter.

iv. **Ferric chloride solution:**

Dissolve 0.25 gram of $FeCl_3.6H_2O$ in distilled water and dilute to one litre.

v. **Manganous sulphate solution:**

Dissolve 480 gram of $MnSO_4$ $4H_2O$ or 400 gram of $MnSO_4.2H_2O$ or 364 gram of $MnSO_4$ H_2O in distilled water and dilute to one litre.

vi. **Alkali Azide reagent:**

Dissolve 500 gram. NaOH (or 700 gram KOH) and 135 gram NaI (or 150 gram KI) in distilled water and dilute to one liter. Add 10 gram NaN_3 dissolved in 40 ml distilled water. Potassium and Sodium salts may be used interchangeably. This reagent should not give Color with starch solution when diluted and acidified.

vii. **0.025 N Sodium thiosulphate solution:**

Dissolve 6.2050 gram $Na_2S_2O_3$. $5H_2O$ in distilled water. Add 0.4 gram solid NaOH and dilute to 1000 ml.

viii. **Starch:**

2 gram lab grade soluble starch and 0.2 gram salicylic acid in 100 ml hot distilled water.

PROCEDURE

- Prepare dilution water in a glass container by bubbling compressed air in distilled water for about 30 minutes.

- Add 1 ml. each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solution for each liter of dilution water and mix thoroughly.

- Adjust pH of dilution water to 7.0 by using NaOH or HCl.

- Add 1 ml of seed for each liter of dilution water.

- Take suitable portion of sample in one liter volumetric flask and dilute to one liter with dilution water, mix thoroughly.

- Fill to BOD bottles (300 ml. each) by above solution.

- Keep one bottle for three days in incubator at 27^{o}C temperature and determine its D.O after three days.

- Determine the D.O content in another bottle immediately.

Determination of Dissolved Oxygen

- Add 2-ml $MnSO_4$ solution and 2 ml of Alkali Azide solution to the sample collected in 300 ml BOD bottle.
- Mix the solution by inverting bottle few times & allow to settle the precipitate.
- Then add 2 ml. Concentrated H_2SO_4 to dissolve precipitate re-stopper the bottle and mix by inverting bottle few times.
- Titrate 203 ml. of above solution with 0.025 N $Na_2S_2O_3$ using starch indicator.
- Similarly for blank, take 2 bottles for dilution water. Determine D.O. content of one bottle immediately and determine D.O. content of another bottle after three days incubation. (at 20^{o}C).

Calculation:

$$\text{BOD mg/litre} = \frac{\mathbf{(D_1 - D_5) - (B_1 - B_3)}}{\text{\% of sample.}}$$

Where:

D_1 = ml of 0.025 N $Na_2S_2O_3$ consumed by sample immediately.

D_5 = 0.025 N $Na_2S_2O_3$ consumed after incubation of Sample for 3 days

B_1 = ml. of 0.025 N $Na_2S_2O_3$ consumed by blank immediately.

B_3 = ml of 0.025 n $Na_2S_2O_3$ consumed after incubation of blank for 3 days

3.2.5 DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD)

PRINCIPLE

Most types of organic matter are oxidized by boiling mixture of chromic and sulfuric acid. A sample is refluxed in strongly acid solution with a known volume of potassium dichromate ($K_2Cr_2O_7$) is titrated with ferrous ammonium sulfate to determine the amount of ($K_2Cr_2O_7$) consumed and the oxidizable organic matter is calculated in terms of oxygen demand. Keep ratings of reagents weights volumes other than 50 ml are used. The standard 2-hr. reflux time may be reduced, it has been shown that a shorter period yield the same results.

OPEN REFLUX METHOD-COD ANALYSIS:

Reagents:

i. **Standard Potassium Dichromate Solution, 0.25N:**

ii. **Sulfuric acid reagent:**

Add Ag_2SO_4 reagent (technical grade, crystals or power) to concentrated H_2SO_4 at the rate of 5.5 gram Ag_2SO_4 /Kg H_2SO_4. Let it stand for 1 to 2 days to dissolve Ag_2SO_4.

iii. **Ferroin indicator solution:**

Dissolve 1.485gram 1,10 – phenanthroline monohydrate and 0.695 gram $FeSO_4$, 7 H_2O in distilled water and dilute to 100 ml. Readymade indicator solution may be purchased.

iv. **Standard Ferrous Ammonium Sulfate:**

Dilute 10.0 ml standard $K_2Cr_2O_7$ to about 100 ml add 30 ml conc. H_2SO_4 and cool. Titrate with FAS titrant using 0.10 to 0.15 ml (2 to 3 drops) ferroin indicator.

$$\text{Molarity of FAS solution} = \frac{\text{Titrated Volume of 0.25 N } K_2Cr_2O_7\text{, ml} \times 0.25}{\text{Volume of FAS used in titration}}$$

v. **Mercuric sulfate, $HgSO_4$ crystals or powder.**

vi. **Sulfamic acid:** Required only if the interference of nitrites is to be eliminated.

vii. **Potassium hydrogen phthalate (KHP) standard:**

Lightly crush and dry potassium hydrogen phthalate to constant weight at 120 ^oC. Dissolve 425 mg in distilled water and dilute to 100 ml. KHP has a theoretical COD of, 1,176 µg O_2/mg and this solution has theoretical COD of 500 µg O_2/mg. This solution is stable when refrigerated up to 3 months in the absence of visible biological growth.

PROCEDURE:

- Place 20 ml sample (for samples with COD 900 mg /L) use smaller sample portion (in case of high COD values) diluted to 20.0 ml in a refluxing flask.
- Add 1 gram $HgSO_4$, several glass beads, and very slowly add 5.0 ml sulfuric acid reagent with mixing .

- Cool while mixing to avoid possible loss of volatile materials. Add 10.0 ml $K_2Cr_2O_7$ solution and mix.
- Attach flask to condensor and turn on cooling water. Add remaining sulfuric acid reagent (25 ml) through open end of condensor. Continue swirling and mixing while adding the sulfuric acid reagent.
- Cover open end of codensor with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 hour.
- Cool and wash down condensor with distilled water. Disconnect reflux condenser and dilute mixtures to about twice its volume with distilled water.
- Cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS using 0.10 to 0.15 ml (2 to 3 drops) ferroin indicator. Although the quantity of ferroin indicator is not critical use the same volume for all titrations. Take as the end point of the titration the first sharp Color change from blue green to reddish brown.

Calculation:

$$\text{COD as mg } O_2/L = \frac{(A-B) \times M \times 8000}{\text{ml sample}}$$

Where A = ml FAS used for blank., B= ml FAS used for sample and M = molarity of FAS.

3.2.6 PROCEDURE FOR THE DETERMINATION OF ADSORBABLE ORGANIC HALIDES (AOX)

The analysis of the AOX is very critical procedure which require high level of expertise. In India only few laboratories including Central Pulp and Paper Research Institute, Saharanpur are having the facility to determine the AOX. DIN method is followed to measure AOX in liquid samples. This is also an instrumentation method. The values obtained include most chlorinated organics and it is reported as organically bound chlorine. The procedure involves the adsorption of chlorinated organics onto activated carbon and then combustion at higher temperature in presence of oxygen followed by micro-coulometric titration of produced halides. This procedure was standardized in Germany in 1985 and known as DIN 38 409 Tail 14 AOX procedure. It has been adopted as a legally enforceable measure for control of chlorinated organic compounds in effluent.

The AOX procedure is considered to be the most suitable for adoption to the pulp mill effluents due to its simplicity, more accuracy and better reproducibility. The values of AOX are generally higher (Average 20%) than the TOCl values due to recovery of volatile chloro-organics. The advantages of AOX over the TOCl method are

- Better reproducibility
- Lower detection limit
- Higher percentage of recovery of volatile chlorinated organic compounds.

Today AOX has been accepted as a standard monitoring and regulatory parameter for pulp and paper mill effluents world wide in preference to TOCl.

PURPOSE:

The test measures the amount of chlorine bonded with organic matters present in aqueous solution, which is absorbable onto the activated carbon.

PRINCIPAL:

The organic halides adsorbed onto the activated carbon decomposed in presence of oxygen at 1000 ± 50 ^{0}C and thus formed hydrogen chloride is precipitated by silver ions in an acetic acid solution in microcoulometric titration cell. The silver ions consumed are replaced electrochemically and the generating current is integrated and displayed digitally as chlorine in test sample.

INTERFERENCE :

The inorganic chlorine contaminants like Cl_2, ClO_2, Cl, ClO_3, ClO etc. contribute positive error to AOX which needs pretreatment and removal of these contaminants. Atmospheric chlorine if present may also contribute a higher AOX values.

REAGENTS

(a.) **Sodium Nitrate Solution:** Dissolve 4.25 gram sodium nitrate in a small amount of distilled water, add 0.4 ml Conc. HNO_3 and makeup to250ml.

(b.) **Washing Solution :** Dilute 50 ml of Nitrate Solution to 1.0 liter with distilled water.

(c.) **Sulfuric Acid:** Add 90 ml Conc. H_2SO_4 to 10 ml distilled water to make 100ml.

(d.) **Standard solution:** Dissolve 0.1103 gram 2-Chlorobenzoic Acid in methanol and make up to 100 ml with methanol.

(e.) **Electrolyte solution:**

APPARATUS :

AOX ANALYZER (ANALYTICKJENA, GERMANY)

Glassware – Beakers, Volumetric flask, Pipettes, Graduated Cylinders, Conical Flasks etc.

3.6.6 OTHER ITEMS -

a) Oxygen gas (99.995%)
b) pH meter
c) Mechanical shaker
d) Polycarbonate membrane filter paper : chloride free or reduced chloride content, diameter 25 mm, pore size 0.4 µm.
e) Vacuum filtration device.
f) Water filter pump or vacuum pump.
g) Forceps for handling of filter paper.
h) Measuring spoon designed for adding required quantity of activated carbon

METHOD:

DIN method is followed to measure AOX in liquid samples. The measurement of AOX involves;

- Pretreatment or Adsorption
- Mineralisation
- Microcoulometric analysis

The details of procedure are as follows:

ANALYSIS :

Homogenise the samples by shaking it before subject to analysis at ambient temperature. Diluted the samples according to the optimum working range of the instrument (25-250 µg/l) and should use minimum volume of 5 ml. of sample for dilution. Then acidify the diluted sample to ~ pH 2 with Nitric acid. Taken 100 ml. acidified sample into Erlenmeyer Stoppard conical flask (250 ml) containing 5 ml of nitrate solution and 50 mg. activated carbon and the flask contents is allowed for shaking for one hour.

After one hour, contents of conical flask were filtered through polycarbonate membrane filter paper followed by nitrate wash to remove the inorganic halides. The loaded activated carbon along with filter paper was integrated and analysed for AOX as per the instructions of AOX analyser manufacturer and give the direct reading according to dilution.

Daily run the blank with dilution water and standard compounds to check the recovery factor. Always run the determination in duplicate.

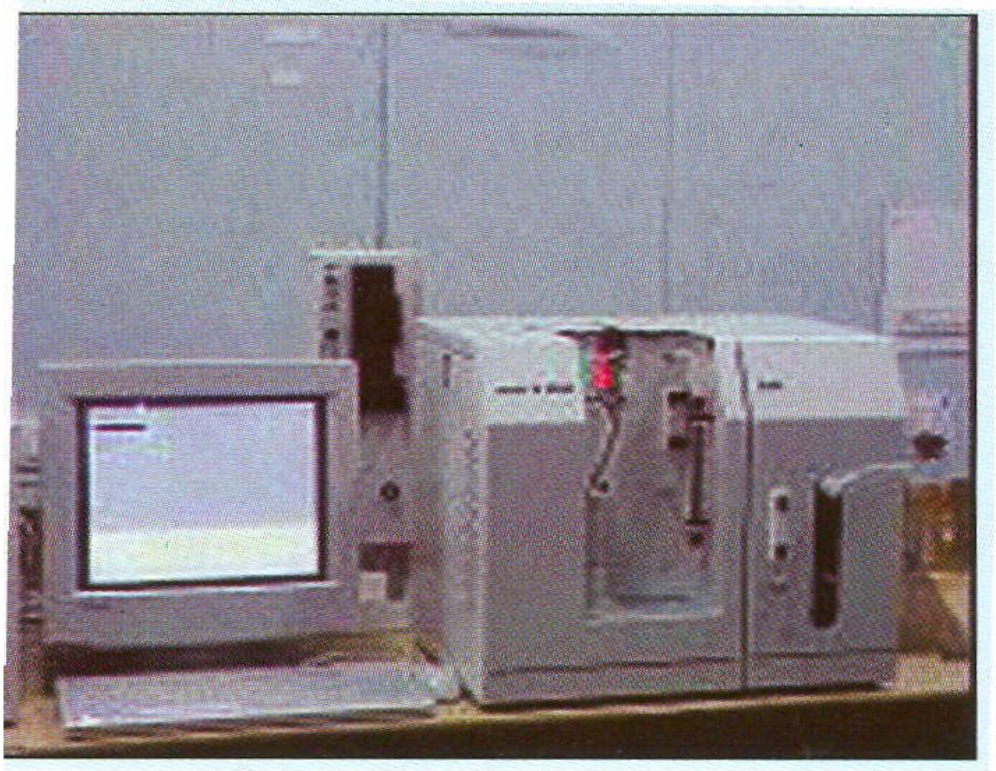

Fig 3.1 - AOX ANALYZER

3.3 GENERATION & CHARACTERIZATION OF BLEACH PLANT EFFLUENTS- LAB SCALE

Studies were initiated with the objective to determine the potential of AOX generation by conventional bleaching of pulp produced from raw materials commonly used in Indian pulp and paper industry i.e. bagasse (Agro), bamboo and eucalyptus. All these three raw material were cooked separately in a laboratory series digestors by using optimized cooking chemical dosage 14, 17.5 and 16% Na_2O respectively. The pulp produced was bleached using conventional bleaching sequence i.e. CEH to achieve the brightness level of 80 % ISO. The bleach effluent generated was analyzed for various pollutional parameters including AOX. The results are indicated in **Table 3.2**.

TABLE-3.2

CHARACTERISATION OF LABORATORY GENERATED COMBINED BLEACH EFFLUENT (CEH)

Raw materials	COD kg/t $_{pulp}$	BOD kg/t $_{pulp}$	AOX kg/t $_{pulp}$
Bagasse (Agro)	40.6	11.3	2.93
Bamboo	43.6	12.8	4.63
Eucalyptus	33.0	8.8	4.18

3.4 MILL STUDIES

3.4.1 CHARACTERISATION OF BLEACH PLANT EFFLUENT COLLECTED FROM THE INDIAN PULP AND PAPER MILLS

The composite bleach plant effluent samples were collected from the wood based mills and agro based mills using conventional bleaching sequence. These samples were characterized for various pollutional parameter main emphasis given on Absorbable Organic Halide (AOX). The raw material of wood based mills were mainly woody mixed raw material and raw material of agro based mills were rice straw and bagasse.

The Characterization of bleach plant effluents collected from agro based mill for different pollution parameters are given in the **Tables- 3.3, 3.4 & 3.5** & characterization of bleach plant effluents collected from wood based mill are given in **Table- 3.6, 3.7 & 3.8.**

TABLE –3.3

CHARACTERIZATION OF BLEACHED PLANT EFFLUENT COLLECTED FROM AGRO BASED MILL

(SAMPLE-1)

Parameters	**C-stage**	**E-stage**	**H-stage**	**Combined bleach effluent**
pH	2.2	9.8	7.3	7.8
TS, mg/l	1550	2408	2135	2212
TSS, mg/l	188	255	174	280
TDS, mg/l	1362	2153	1961	1932
COD, mg/l	888	1920	920	1812
BOD_3 mg/l	315	750	448	672
Color, PCU	315	3820	150	2720
Chloride, mg/l	758	354	1615	575
Lignin, mg/l	100	566	73	240
Organic, %	55	45	50	42
Inorganic, %	45	55	50	58
AOX, mg/l	**78.2**	**98.4**	**45.5**	**76.4**

TABLE –3.4

CHARACTERIZATION OF BLEACHED PLANT EFFLUENTCOLLECTED FROM AGRO BASED MILL

(SAMPLE-2)

Parameters	**C-stage**	**E-stage**	**H-stage**	**Combined bleach effluent**
pH	2.5	10.2	7.1	7.8
TS, mg/l	1602	2320	4309	2162
TSS, mg/l	583	201	380	230
TDS, mg/l	1019	2119	3929	1932
COD, mg/l	972	1489	1985.	1405
BOD_3 mg/l	425	610	808	502
Color, PCU	340	3760	152	1410
Chloride, mg/l	750	340	1437	562
Lignin, mg/l	97.11	505.3	72.0	232.6
Organic, %	53.5	45.6	47.8	46.0
Inorganic, %	46.5	54.4	52.2	54.0
AOX, mg/l	**71.4**	**95.0**	**47.7**	**55.0**

TABLE –3.5

CHARACTERIZATION OF BLEACHED PLANT EFFLUENT COLLECTED FROM AGRO BASED MILL

(SAMPLE-3)

Parameters	C-stage	E-stage	H-stage	Combined bleach effluent
pH	2.2	9.8	7.2	7.5
TS, mg/l	1512	2410	3010	2162
TSS, mg/l	485	252	188	412
TDS, mg/l	1027	2158	2822	1750
COD, mg/l	988	2280	1252	1610
BOD_3, mg/l	230	810	520	690
Color, PCU	390	4180	155	1200
Chloride, mg/l	788	325	1410	590
Lignin, mg/l	92	500	55	242
Organic, %	55	51	45	52
Inorganic, %	45	49	55	48
AOX, mg/l	**83.4**	**109.4**	**64.8**	**68.6**

TABLE –3.6

CHARACTERIZATION OF BLEACHED PLANT EFFLUENT COLLECTED FROM WOOD BASED MILL

(SAMPLE-1)

Parameters	C-stage	E-stage	H-stage	Combined bleach effluent
pH	2.6	8.5	6.3	5.5
TS, mg/l	2450	3600	6280	2640
TSS, mg/l	1208	69	150	206
TDS, mg/l	1242	3531	6130	2434
COD, mg/l	888	1810	828	1305
BOD_3, mg/l	140	430	340	380
Chloride mg/l	820	740	1610	1124
Color, PCU	356	3750	344	1026
Organic, %	42.5	43	41.5	43
Inorganic, %	57.5	57	58.5	57
Lignin, mg/l	88	600	145	378
AOX, mg/l	**55.0**	**98.5**	**46.2**	**58.3**

TABLE –3.7

CHARACTERIZATION OF BLEACHED PLANT EFFLUENT COLLECTED FROM WOOD BASED MILL

(SAMPLE-2)

Parameters	C-stage	E-stage	H-stage	Combined bleach effluent
pH	2.5	7.0	6.6	5.0
TS, mg/l	3200	3460	6940	2970
TSS, mg/l	1470	70	110	181
TDS, mg/l	1789	3390	6820	2900
COD, mg/l	1252	1598	1020	1411
BOD_3, mg/l	160	691	350	614
Chloride, mg/l	759	766	2537	1089
Color, PCU	305	3460	424	1650
Organic, %	46.5	42.7	42.7	44.3
Inorganic, %	43.5	57.3	57.3	55.7
Lignin, mg/l	96	595	158	390
AOX, mg/l	**41.4**	**87.9**	**45.5**	**50.7**

TABLE –3.8

CHARACTERIZATION OF BLEACHED PLANT EFFLUENT COLLECTED FROM WOOD BASED MILL

(SAMPLE-3)

Parameters	C-stage	E-stage	H-stage	Combined bleach effluent
pH	2.2	8.96	5.5	5.9
TS, mg/l	1850	2855	5208	2010
TSS, mg/l	850	80	310	124
TDS, mg/l	100	2775	4898	1886
COD, mg/l	1248	2488	1050	1284
BOD_3, mg/l	160	380	300	424
Chloride, mg/l	722	758	2522	1142
Color, PCU	310	3442	436	2628
Organic, %	46	42	46	44.8
Inorganic, %	54	58	54	55.2
Lignin, mg/l	88	600	162	370
AOX, mg/l	**52.5**	**88.3**	**59.6**	**52.0**

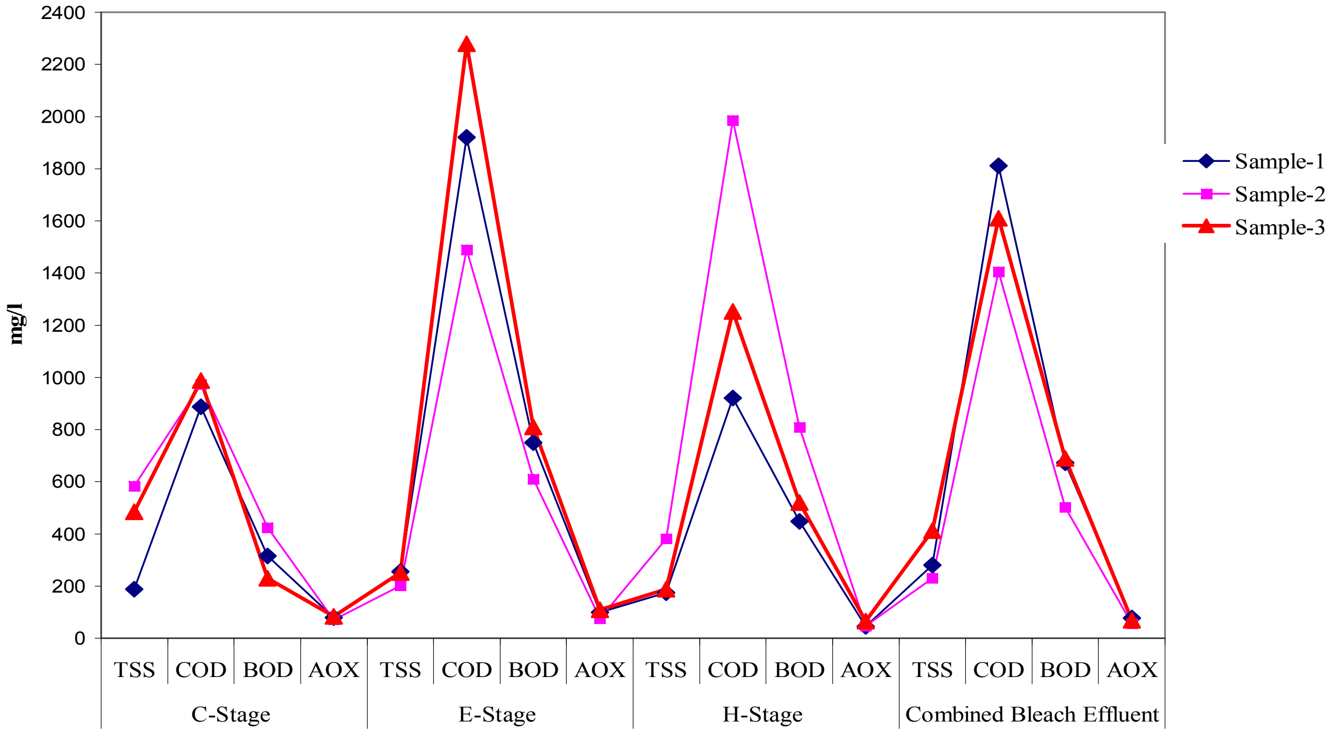

Fig 3.2 - Pollution Load Generation in Agro Based Mill

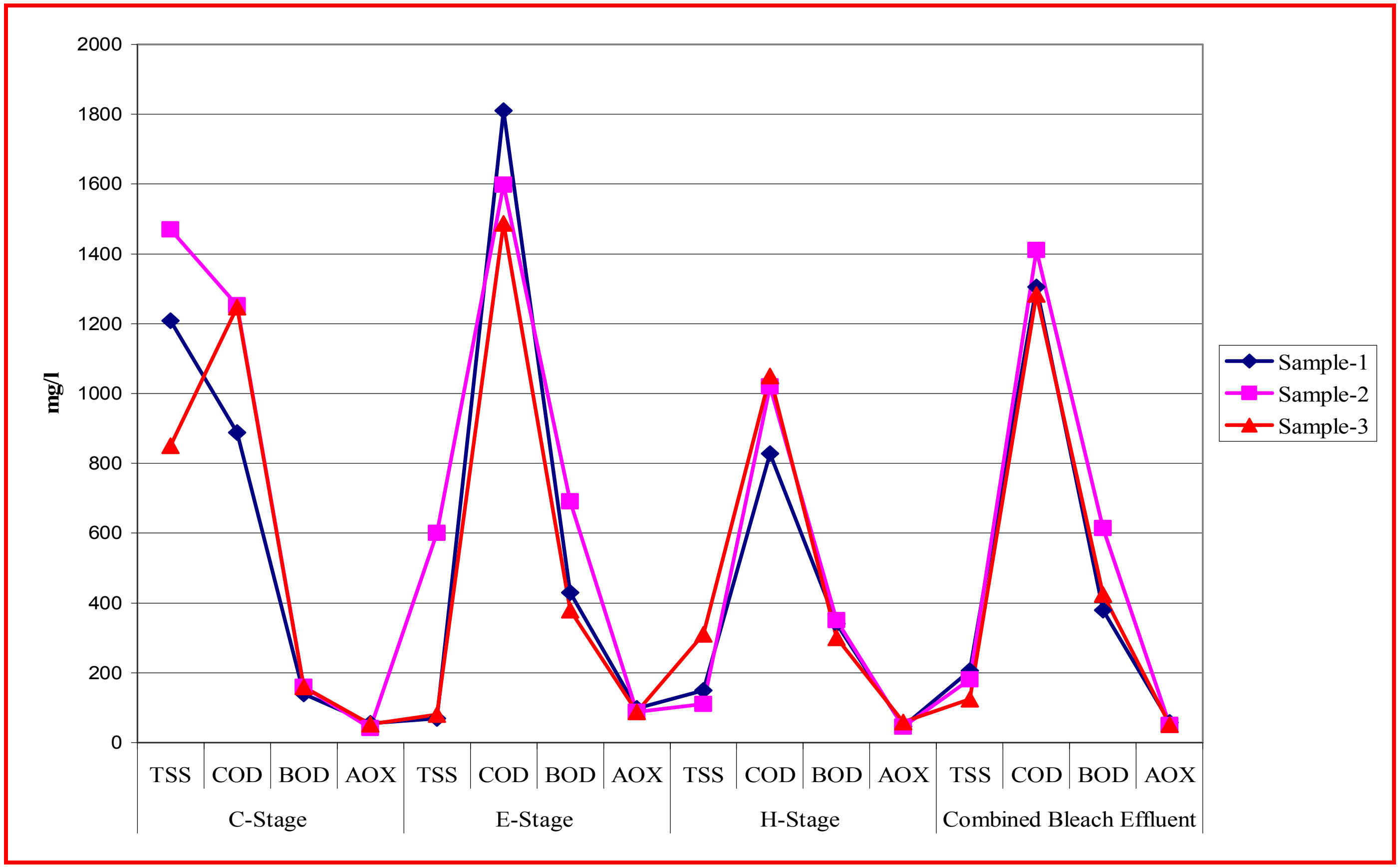

Fig 3.3 - Pollution Load Generation in Wood Based Mill

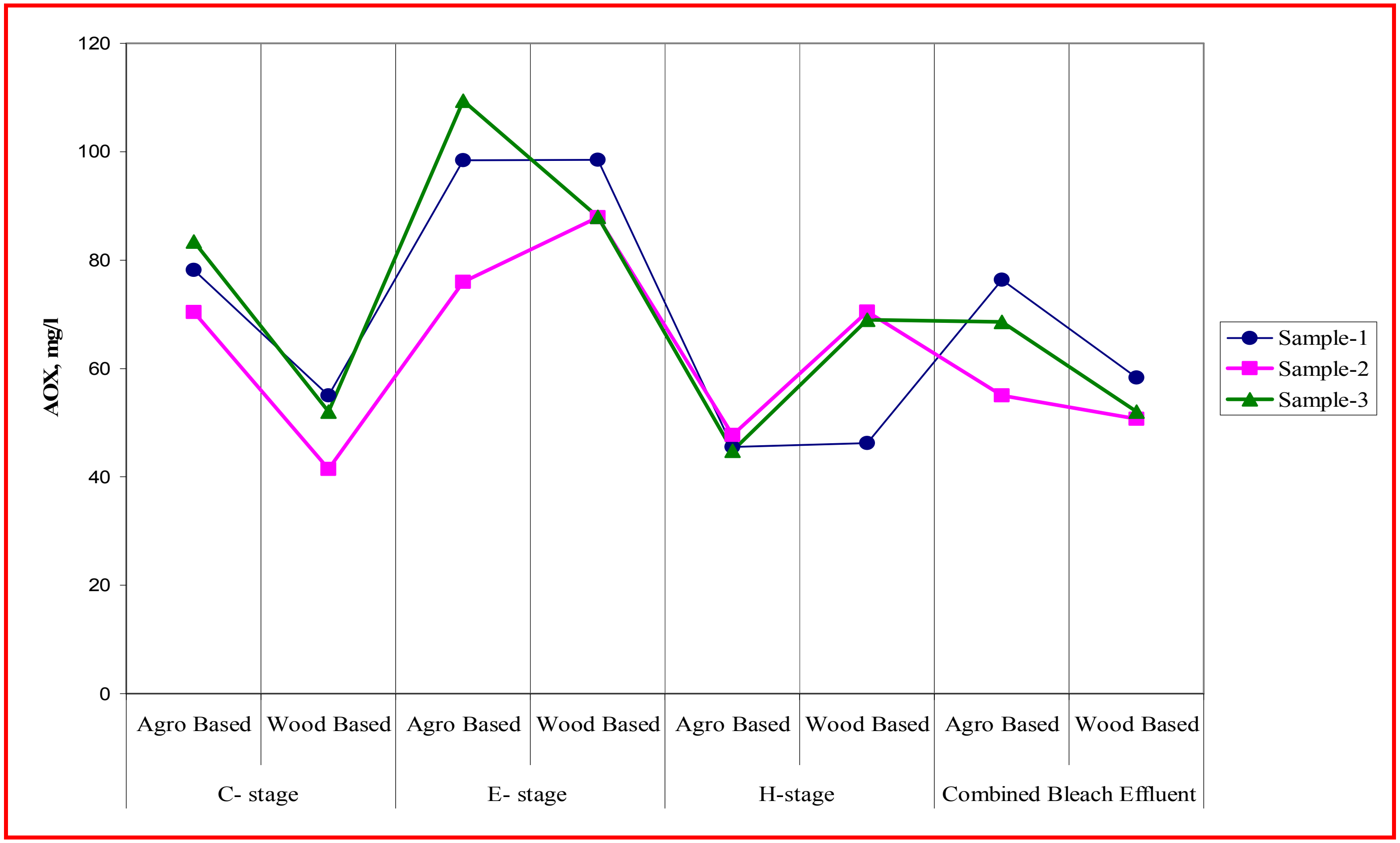

Fig 3.4 – AOX Load Generation in Agro & Wood Based Mill

CHAPTER- 4.0

TOXICITY EVALUATION OF BLEACH PLANT EFFLUENT

The chapter include the toxicity level of different bleach plant effluents collected from large wood based and small agro based mills are studied.

Toxicity is a relative property of chemical which refers to its potential harmful effect on the living organisms. It is a function of the concentration of chemical and duration of exposure.

There are various ways to recognize the toxicity. On the basis of the nature of toxic effect of chemical, there are recognized acute and chronic effects.

Acute toxicity- the effects are directly related to the ingestion of the chemical. These effects occur rapidly as result of short term exposure of few hours, days or weeks to a chemical. Generally, acute effects are relatively severe the most common being lethality or mortality.

Chronic toxicity – there is often an ingestion of small quantities of the toxic chemical over prolonged period of time leading to toxic concentrations and thus symptoms of poisoning. These effects are therefore a consequence of repeated or long term exposure.

For a chemical, its metabolite have a toxic effect on the biological organisms. The compound must come in contact and react with an appropriate part of the organisms at a high enough concentration and for a required duration of time. The toxicity effects vary with chemical, species of organisms and severity of effects. The most important factor for toxicity assessment is duration & frequency of exposure and chemical concentration.

The earliest concern about the effects of AOX in the aquatic environment were identified in Swedish attributing population declines among biota in Baltic sea to discharge from pulp and paper mills that use chlorine bleaching.

4.1 FISH TOXICITY

Toxicity test is used to determine the potential harmful impact of wastewater on aquatic ecosystems. Toxicity test is also helpful to estimate the toxic impacts of different chemicals, often fluctuating, untreated wastewater on activated sludge waste water treatment process. The conventional bleaching process followed by Indian pulp and paper industry, thus discharging high level of chlorophenolic compounds (AOX) which are toxic to the aquatic organism. Fish are particularly susceptible to the influence of toxic substance during the reproductive and early stages of development. Determination of the influence on early developmental stages is a more sensitive index of fish tolerance than obtained by determination of acute toxicity. The test fish species used should be selected on the basis of practical criteria, such as their ready availability throughout the year, ease of maintenance, convenience for testing, relative sensitivity to chemicals, and economic, biological or ecological factors which have any bearing.

Three types of procedure can be used:

Static test:

Toxicity test in which no flow of test solution occurs. (Solutions remain unchanged throughout the duration of the test)

Semi-static test:

Test without flow of test solution, but with regular batch wise renewal of test solutions after prolonged periods.

Flow-through test:

Toxicity test in which the water is renewed constantly in the test chambers, the chemical under test being transported with the water used to renew the test medium.

The purpose of this laboratory exercise was to study the effects of different concentrations of an “effluent” on aquatic organisms in order to find out when these concentrations reach dangerous levels.

4.1.1 EXPERIMENTAL WORK

STATIC TEST:

The toxicity of bleach plant effluents collected from mills to Common Carp Fish (*Cyprinus carpio*) were tested according to standard method ((ISO 7346-1 1996 & IS: 6582 - 1971). The procedure is based upon direct exposure to fish to measure LC_{50} under controlled laboratory condition.

The fish of weighing 5-6 gram and length 4-5 cm were purchased from a local fish hatchery. Prior to use, the fish were acclimated for 12 days to laboratory well water at a temperature 25+ 3 ^{o}C, at pH of 7.7, hardness of 210 mg/l. The same well water was used for effluent dilution purposes. Dissolved oxygen concentrations were maintained above 90% saturation with oil free compressed air. The fish were fed a commercial diet at a daily rate of 1% body weight. Feeding were stopped 48 hours before the beginning of each exposure.

Exposures lasting 96h were conducted in glass aquarium of 20 liter capacity at a temperature of 25±3 ^{o}C. 10 - 20 fish of approximately the same weight and length were placed in aquaria containing effluents. The fish were not fed during experiments and all other parameters were monitored daily like measurements of pH, dissolved oxygen and temperature are carried out daily. The fish were inspected after the first 2 to 4 hours and at least at 24-hour intervals. Fish were considered dead if touching of the caudal peduncle produces no reaction, and no breathing movements were visible. Dead fish were removed when observed and mortalities were recorded

4.1.1.1 WOOD BASED MILL

Toxicity of bleach plant effluents (C-stage, E-stage, H-stage & combined) collected from a wood based mill through 3 different composite sampling were determined by using bioassay technique in lab scale aquarium using fish and results obtained are shown in **Table 4.1, 4.2, 4.3 & 4.4.**

TABLE-4.1

TOXICITY POTENTIAL OF C-STAGE EFFLUENT

(WOOD BASED MILL)

Test condition

D.O. ,mg/l – 7.3 – 7.7

Temperature, ^{o}C - 25$\underline{+}$2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	30	20	30
50	70	40	60
70	80	70	90

TABLE- 4.2

TOXICITY POTENTIAL OF E-STAGE EFFLUENT
(WOOD BASED MIL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25± 2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	40	30	50
50	80	70	70
70	90	70	90

TABLE- 4.3

TOXICITY POTENTIAL OF H-STAGE EFFLUENT
(WOOD BASED MILL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25± 2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	20	25	30
50	40	35	40
70	60	55	70

TABLE- 4.4

TOXICITY POTENTIAL OF COMBINED BLEACH EFFLUENT (WOOD BASED MILL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25± 2

Effluent Concentration, %	**%Fish Mortality after 96hr (Sample-1)**	**%Fish Mortality after 96hr (Sample-2)**	**%Fish Mortality after 96hr (Sample-3)**
0	0	0	0
30	20	30	20
50	50	65	45
70	70	75	70

4.1.1.2 AGRO BASED MILL

Toxicity of bleach plant effluents (C-stage, E-stage, H-stage & combined) collected from an agro based mill through 3 different composite sampling were determined by using bioassay technique in lab scale aquarium using fish and results obtained are shown in **Table. – 4.5, 4.6, 4.7 & 4.8.**

TABLE-4.5

TOXICITY POTENTIAL OF C-STAGE EFFLUENT (AGRO BASED MILL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25±2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	40	35	45
50	70	65	70
70	90	75	85

TABLE- 4.6

TOXICITY POTENTIAL OF E-STAGE EFFLUENT (AGRO BASED MILL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25±2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	45	50	50
50	75	70	80
70	90	85	100

TABLE-4.7

TOXICITY POTENTIAL OF H-STAGE EFFLUENT (AGRO BASED MILL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25± 2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	30	35	30
50	55	55	65
70	65	70	70

TABLE-4.8

TOXICITY POTENTIAL OF COMBINED BLEACH EFFLUENT (AGROBASED MILL)

Test condition

D.O., mg/l – 7.3 – 7.7

Temperature, °C - 25± 2

Effluent Concentration, %	%Fish Mortality after 96hr (Sample-1)	%Fish Mortality after 96hr (Sample-2)	%Fish Mortality after 96hr (Sample-3)
0	0	0	0
30	40	30	30
50	60	70	60
70	85	80	80

4.1.2 ACUTE TOXICITY (LC_{50})

Acute toxicity is the discernible adverse effect induced in an organism within a short time (days) of exposure to a substance. In the present study, acute toxicity has been expressed as the median lethal concentration (LC_{50}), which were the concentration in water which kills 50% of a test batch of fish within a continuous period of exposure which must be stated.

LC_{50} value of the fish toxicity of Bleach Plant Effluents collected from wood based and agro based mill are given in the **Table 4.9 & 4.10 Fig 4.2 -4.11.**

TABLE-4.9

FISH TOXICITY (LC_{50} VALUE) OF BLEACH PLANT EFFLUENTS OF WOOD BASED MILL

	Volume Concentration of Effluent, %			
Sample Particular	**C-Stage**	**E-Stage**	**H-Stage**	**Combined Bleach Plant Effluent**
Sample- 1	40	35	60	50
Sample- 2	50	40	65	42
Sample- 3	44	30	57	55

TABLE-4.10

FISH TOXICITY (LC_{50} VALUE) OF BLEACH PLANT EFFLUENTS OF AGRO BASED MILL

	Volume Concentration of Effluent, %			
Sample Particular	**C-Stage**	**E-Stage**	**H-Stage**	**Combined Bleach Plant Effluent**
Sample- 1	37	34	47	40
Sample- 2	40	33	45	40
Sample- 3	35	30	43	44

4.2 MICROTOX TOXICITY

In recent years various bacterial bioassys have been developed for screening of wastewater toxicity, most of them are based on the measurements of growth inhibition, respiration and viability of bacterial cells. Microorganisms, bacteria in particular , have several attributes which make them attractive for use in wastewater toxicity testing. Microbial tests are simple, rapid and sensitive. With these tests it is possible to estimate the harmful effects of wastewaters on natural aquatic microbes. By using bacterial toxicity tests it is also possible to estimate the toxic impacts of different, often fluctuating, untreated wastewaters on activated sludge wastewater treatment process.

Toxicity inhibition response of bleach plant effluents on Luminescent bacteria (*Vibrio fisheri*) were also evaluated using **Microtox Toxicity Analyser.** Microtox Toxicity Analyser is widely used in developed countries to assess toxicity emission factor and also to establish a correlation between conventional LC_{50} & instrumental Microtox toxicity.

4.2.1 PRINCIPLE

The inhibition of light production of Vibrio fischeri luminescent bacteria indicates disturbance of the energy metabolism of this heterotrphic bacterium. Because this luminescent pathway is direct branch of electron transport chain the luminescent measurement assesses the metabolic status of this bacterium. Hence the change in bacterial luminescence when these bacteria are exposed to wastewater samples can be used as an indicator of potential toxicity (J.Ahtianien et al.). The sensitivity of the microtox method has been proven to be comparable to acute toxicity tests with fish and crustaceans in several comparative investigations (B.Eklund et al.)

The toxicity of the effluents were also tested according to the standardized luminescence bacteria test procedure (DIN 38412 Teil 34 1991) by *ToxAlert* 10 instrument. Comparison of Microtox Toxicity with other toxicity tests has pointed out the satisfactory sensitivity of microtox for analyzing the toxicity of pulp and paper mill effluents (Juha Fiskari and Pertti K. Hynninen 2000). The luminescence inhibition tests were accomplished by combining bleach effluents collected from wood and agro based mills with the luminescence bacteria *Vibrio fischeri* NRRL B-11177.

The luminescent bacteria such as *Vibrio fischeri* naturally emit light. The enzyme involved is bacterial luciferase which catalyses the following reaction:

$$\mathrm{FMNH_2 + O_2 + R\text{-}CO\text{-}H \longrightarrow FMN + R\text{-}COOH + H_2O +}$$
$$\text{Light (490nm)}$$

Bioluminescence is directly proportional to the metabolic status of the cell. A toxic substance will causes changes to the cellular state, which may be in different level like cell wall, cell membrane, the electron transport chain, enzymes, cytoplasmic constituent, in all these cases changes are rapidly reflected in a decrease in bioluminescence. The decrease of light is measured with a photomultiplier in a luminometer. This light reduction is equal to the toxicity of sample.

4.2.2 REAGENT FOR THE TOXALERT

i) Freeze-dried photo bacteria reagents, *Vibrio fischeri* NRRL B-11177

ii) Control Solution, 2% saline solution

iii) Reconstitution Medium

All reagents were from the instrument supplier (Merck)

4.2.3 PROCEDURE

Sample was prepared by adding the 2 gram NaCl per 100 ml sample.

The bottle of reconstitution medium & control solution were allowed to equilibrate to ambient temperature.

One ml. of reconstitution medium was added to the measurement cuvettes containing the reagents in row A of the sample rack and kept for 20 minutes.

Place an empty measurement cuvette in rack C of the sample rack. Position the cuvette such that it accompanies the cuvette in row A.

Turn on the ToxAlert Luminometer and select SIN mode.

When the reconstitution period of 20 minutes elapsed, mix the content of the measurement cuvette in row A and transfer 0.5 ml reagent to accompanying vial in row C.

Shake the Control solution well and add 0.5 ml to the measurement cuvette in row A and press OK on the luminometer. A count time appear.

After 30 seconds add 0.5 ml sample solution to accompanying cuvette in row C, and discard the pipette tip.

Place the measurement cuvette containing the control solution in row A into the luminometer, and at 15 minutes press load. The instrument will eject the cuvette when the measurement is complete. Return the cuvette to the original position in the rack.

Place the cuvette containing the sample in row C in to the luminometer and at 15 minutes 30 second press load. The instrument will automatically eject the cuvette when the measurement is complete. Return the cuvette in to the original position in the rack.

The % inhibition will be displayed on the screen.

The samples where bioluminescence inhibition values are less than 25% are considered non toxic samples.

Fig 4.1 - MICROTOX TOX ALERT

The luminescence inhibition (I%) of bleach effluent (C-stage, E-stage, H-stage & combined) collected from wood based mill were measured. The results obtained are summarized in **Table- 4.11 & Fig- 4.12**

TABLE- 4.11

MICROTOX TOXICITY OF LUMINESCENT BACTERIA (% INHIBITION) OF WOOD BASED MILL EFFLUENTS

	% Inhibition			
Sample Particular	**C-Stage**	**E-Stage**	**H-Stage**	**Combined Bleach Plant Effluent**
Sample-1	70	85	50	65
Sample-2	75	90	55	65
Sample-3	65	85	50	70

The luminescence inhibition (% I) of bleach effluent (C-stage, E-stage, H-stage & combined) collected from agro based mill were measured. The results obtained are summarized in **Table- 4.12 & Fig- 4.13.**

TABLE-4.12

MICROTOX TOXICITY OF LUMINESCENT BACTERIA (% INHIBITION) OF AGRO BASED MILL EFFLUENTS

	% Inhibition			
Sample Particular	**C-Stage**	**E-Stage**	**H-Stage**	**Combined Bleach Plant Effluent**
Sample-1	80	95	52	68
Sample-2	75	85	65	75
Sample-3	70	95	60	70

4.3 COMPARISON OF FISH TOXICITY & MICROTOX TOXICITY OF LUMINESCENT BACTERIA (% INHIBITION)

In the **Table – 4.13** & **Table – 4.14** and **Fig – 4.14 & 4.15** shows the relation between the fish toxicity & microtox toxicity of luminescent bacteria (% inhibition) of bleach plant effluents. Higher the % inhibition and lower the LC_{50} is having the high toxic effluent and lower the % inhibition and higher the LC_{50} is having less toxic effluents.

TABLE-4.13

FISH TOXICITY (LC_{50} VALUE) & MICROTOX TOXICITY OF LUMINESCENT BACTERIA (% INHIBITION) OF BLEACH PLANT EFFLUENTS OF WOOD BASED MILL

		Sample-1	**Sample-2**	**Sample-3**
C-Stage	% Inhibition	70	75	65
	LC_{50}	40	50	44
E-Stage	% Inhibition	85	90	85
	LC_{50}	35	40	30
H-Stage	% Inhibition	50	55	50
	LC_{50}	60	65	57
Combined Bleach Effluent	% Inhibition	65	65	70
	LC_{50}	50	42	55

TABLE-4.14

FISH TOXICITY (LC$_{50}$ VALUE) & MICROTOX TOXICITY OF LUMINESCENT BACTERIA (% INHIBITION) OF BLEACH PLANT EFFLUENTS OF AGRO BASED MILL

		Sample-1	**Sample-2**	**Sample-3**
C-Stage	% Inhibition	80	75	70
	LC$_{50}$	37	40	35
E-Stage	% Inhibition	95	85	95
	LC$_{50}$	34	33	30
H-Stage	% Inhibition	52	65	60
	LC$_{50}$	47	45	43
Combined Bleach Effluent	% Inhibition	68	75	77
	LC$_{50}$	40	40	44

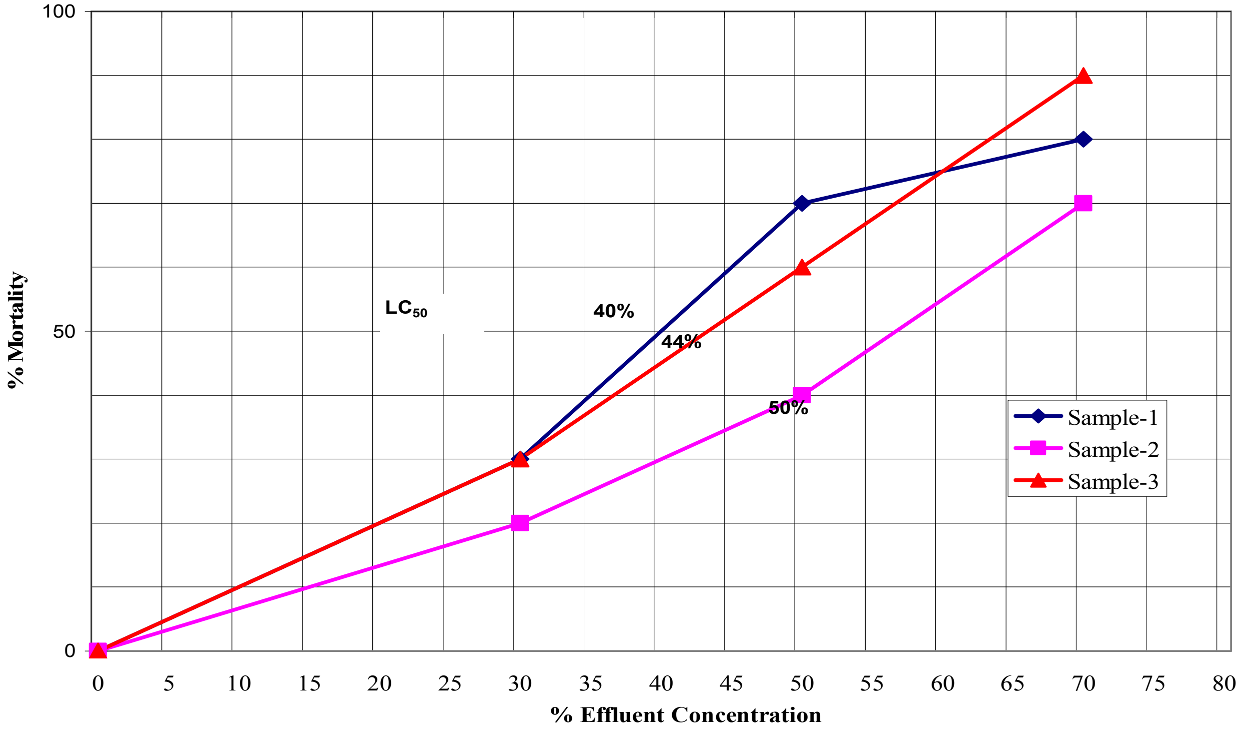

Fig 4.2 - Fish Mortality in C-Stage Effluent of Wood Based Mill

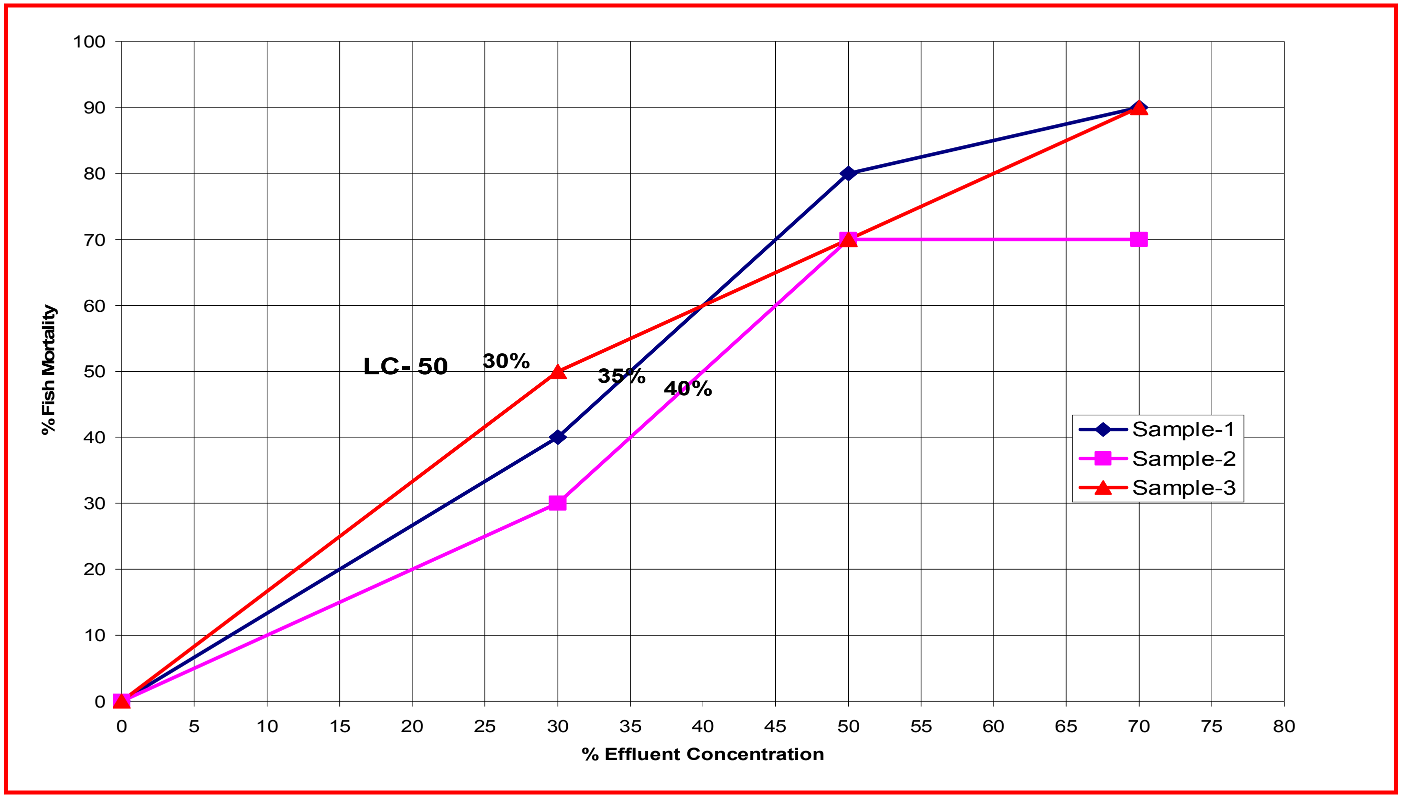

Fig 4.3 - Fish Mortality in E-Stage Effluent of Wood Based Mill

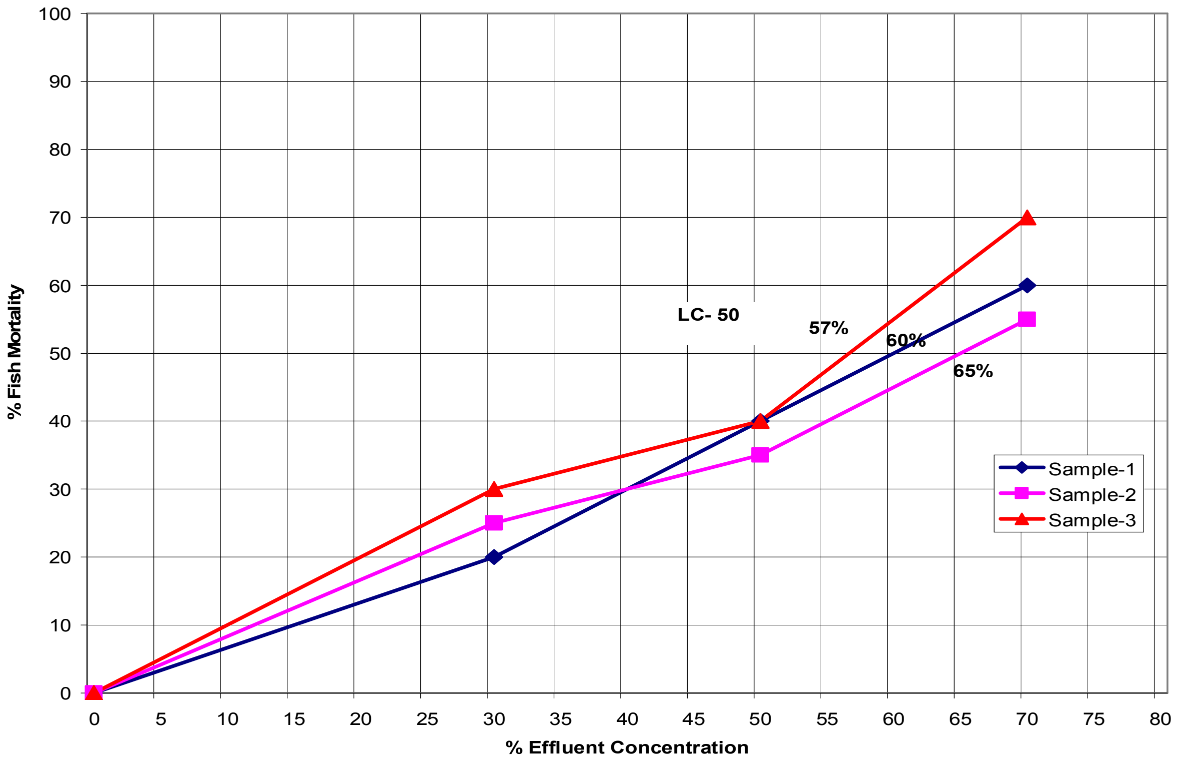

Fig 4.4 - Fish Mortality in H-Stage Effluent of Wood Based Mill

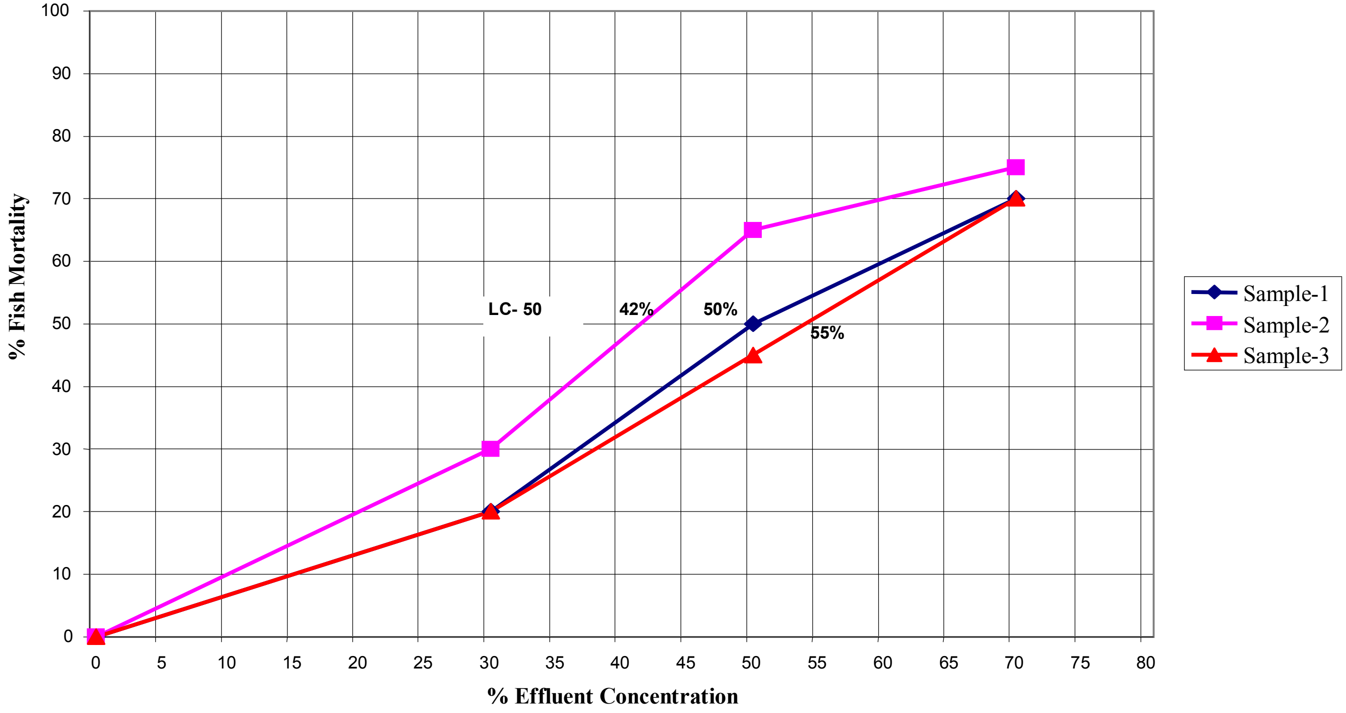

Fig 4.5 - Fish Mortality in Combined Bleach Effluent of Wood Based Mill

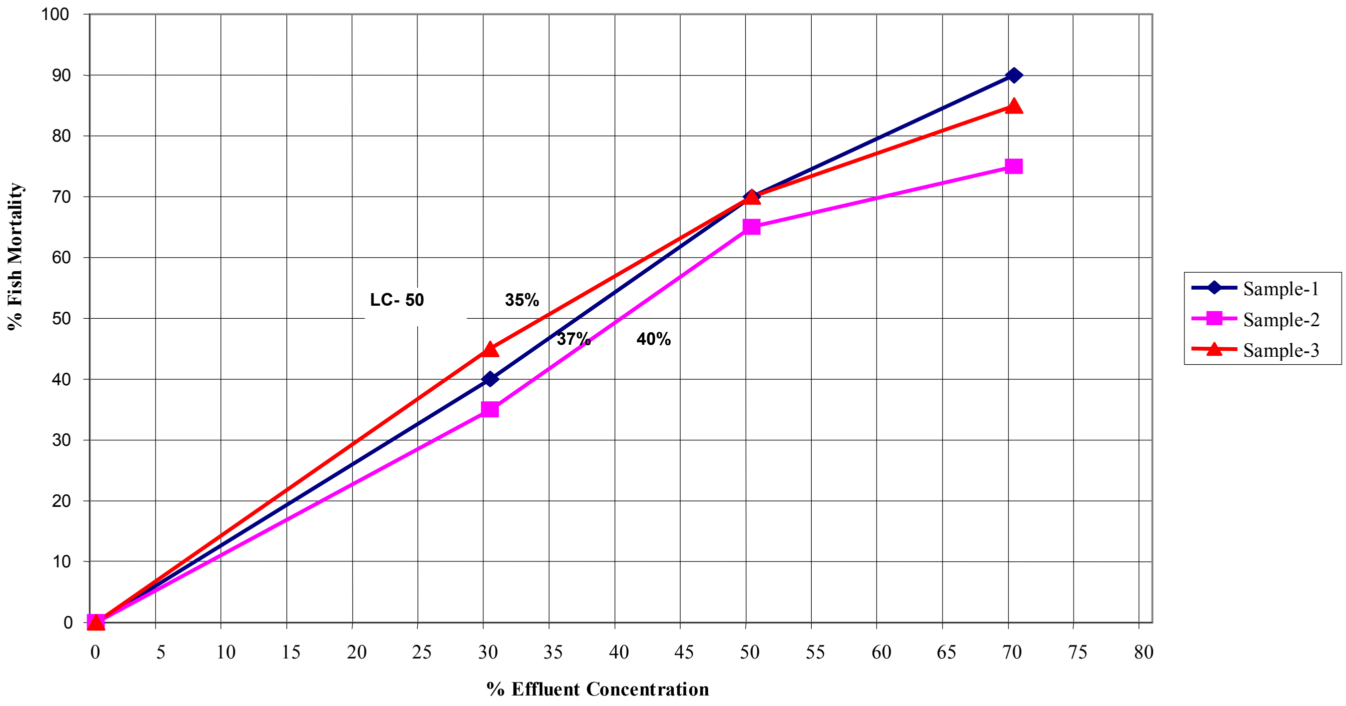

Fig 4.6 - Fish Mortality in C-Stage Effluent of Agro Based Mill

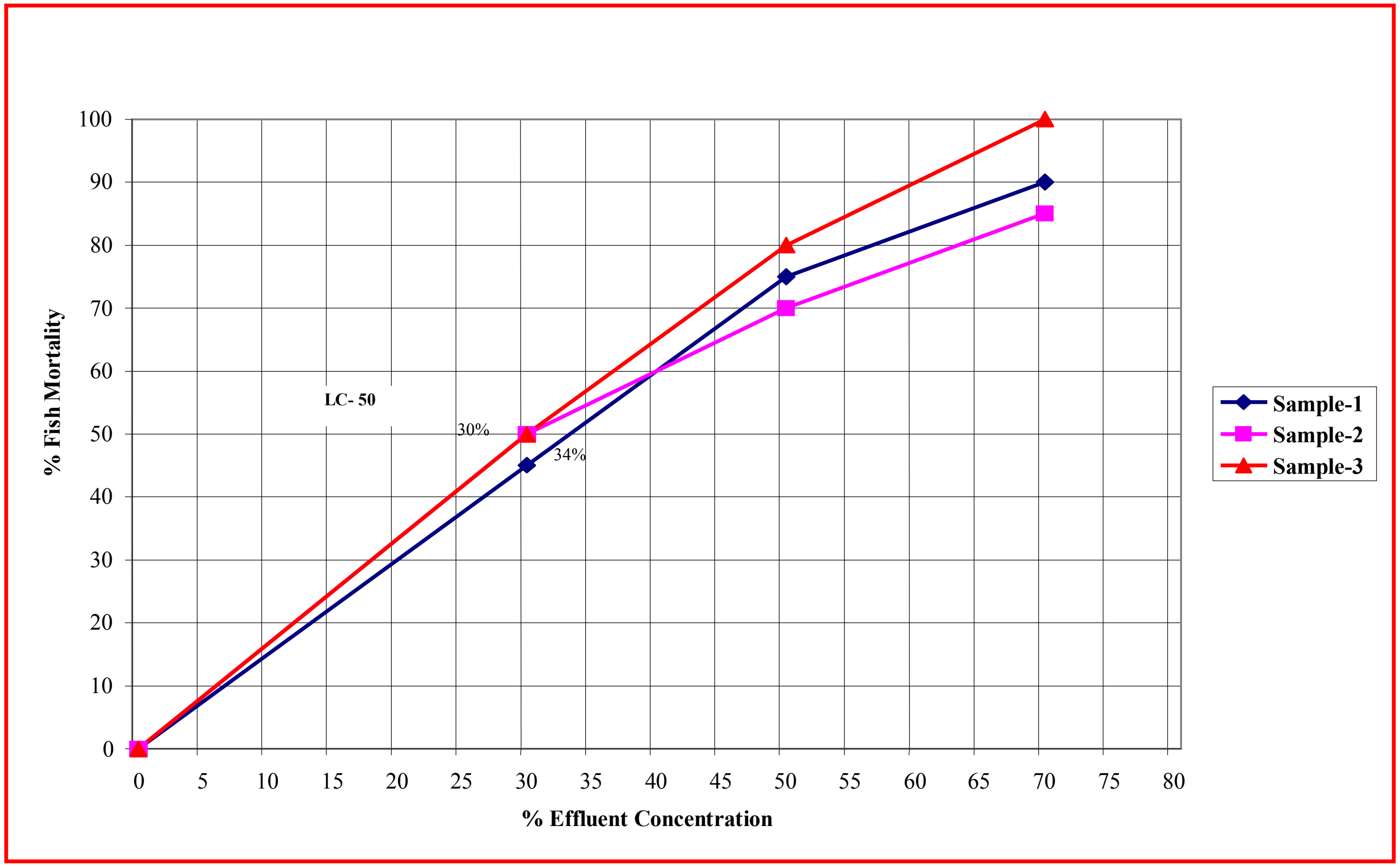

Fig 4.7 - Fish Mortality in E-Stage Effluent of Agro Based Mill

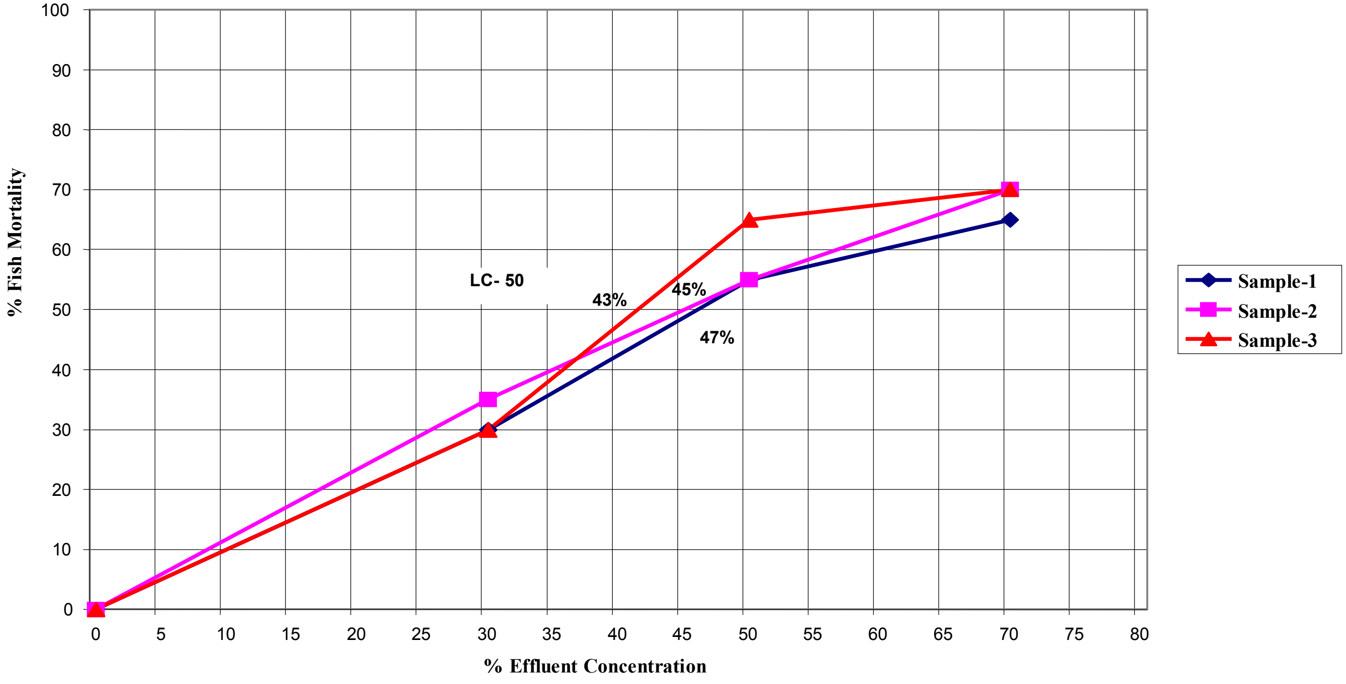

Fig 4.8 - Fish Mortality in H-Stage Effluent of Agro Based Mill

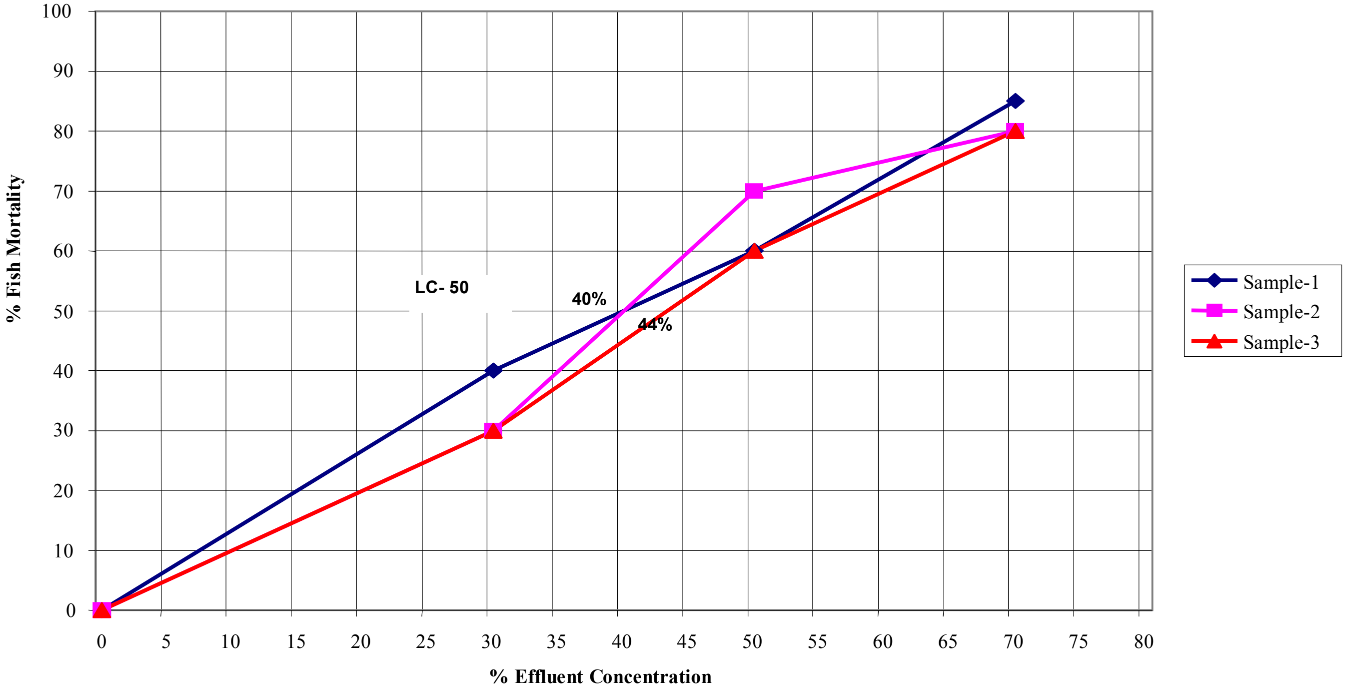

Fig 4.9 - Fish Mortality in Combined Bleach Effluent of Agro Based Mill

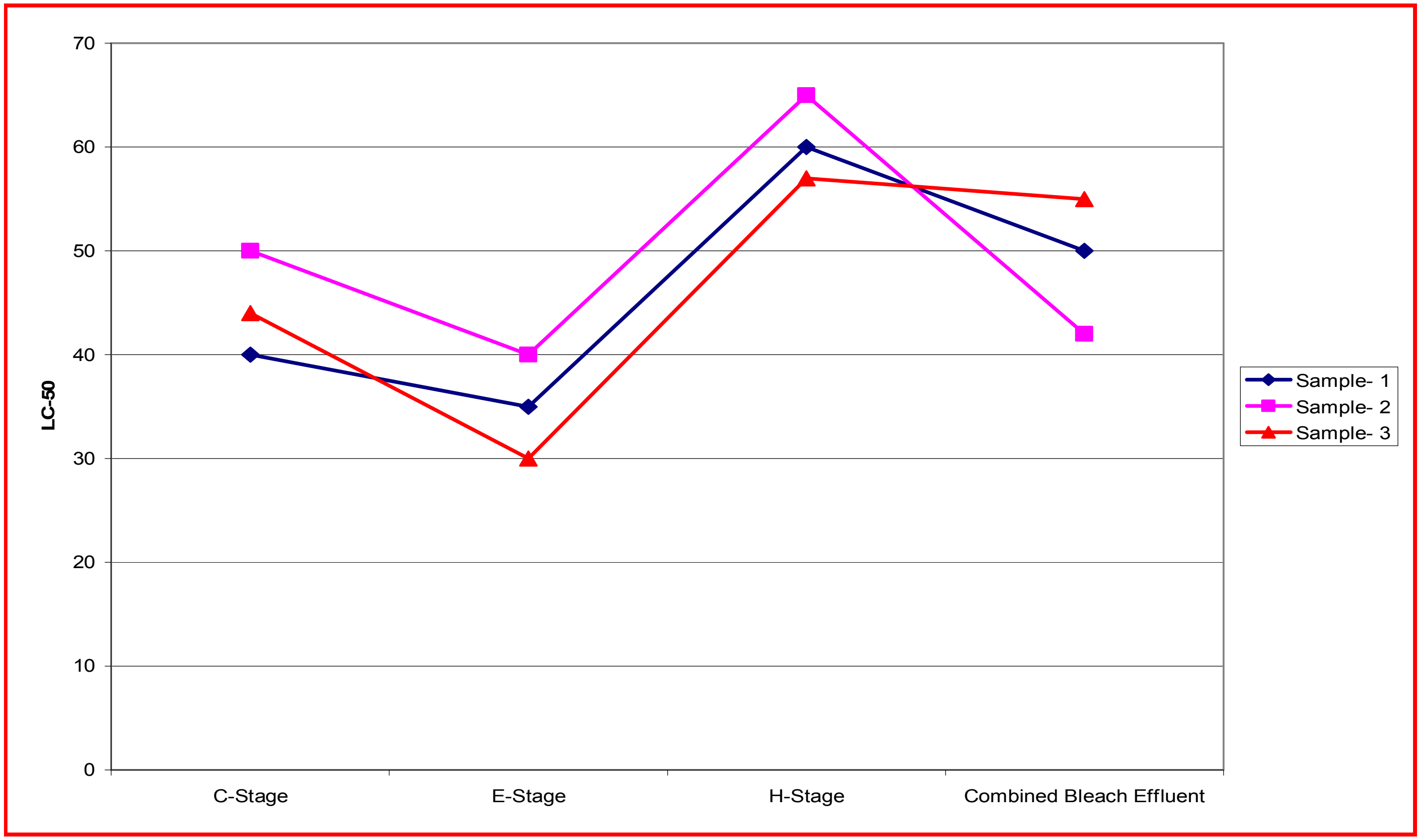

Fig 4.10 - LC_{50} Value of Bleach Plant Effluents of Wood Based Mill

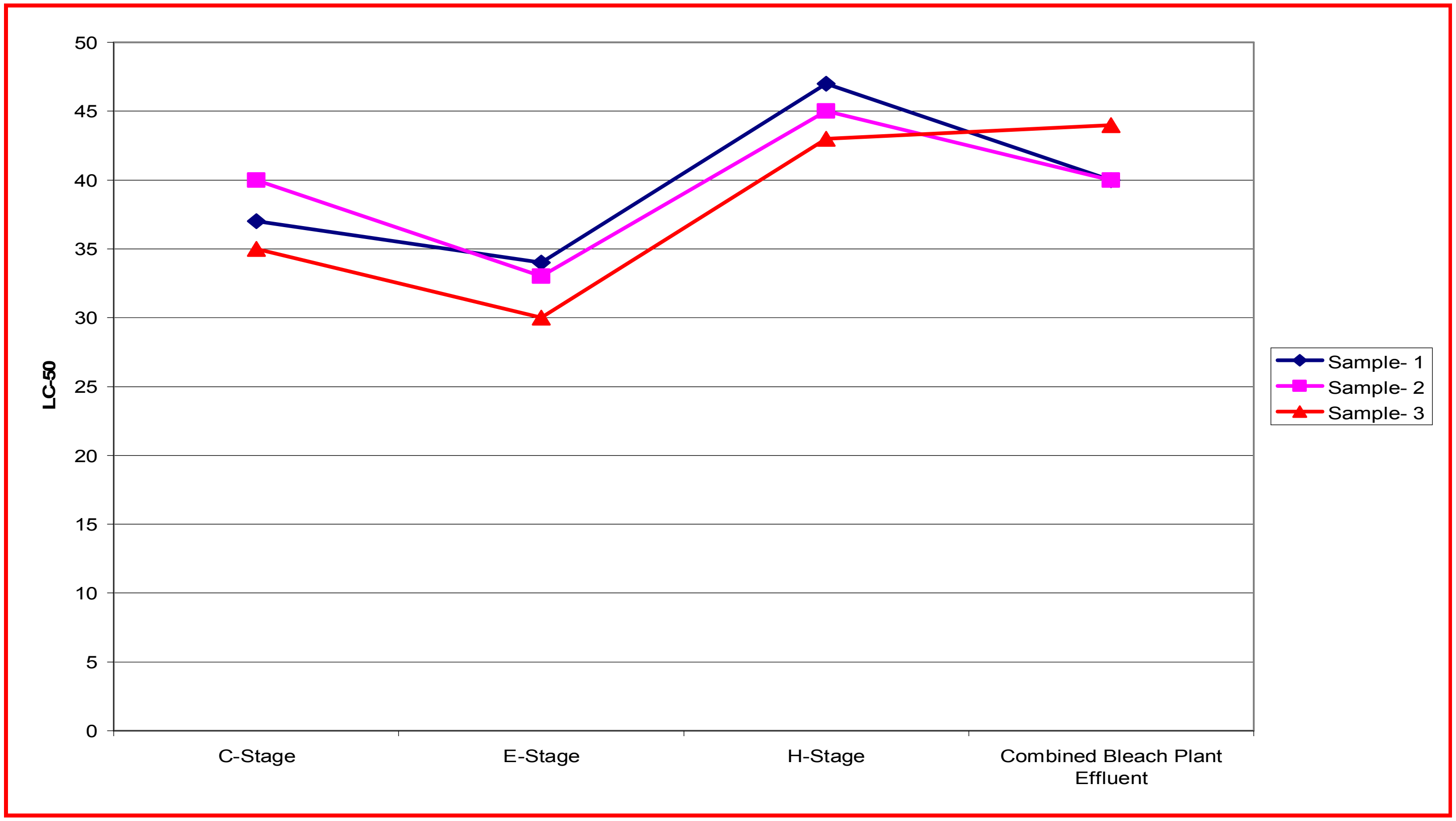

Fig 4.11 - LC$_{50}$Value of Bleach Plant Effluents of Agro Based Mill

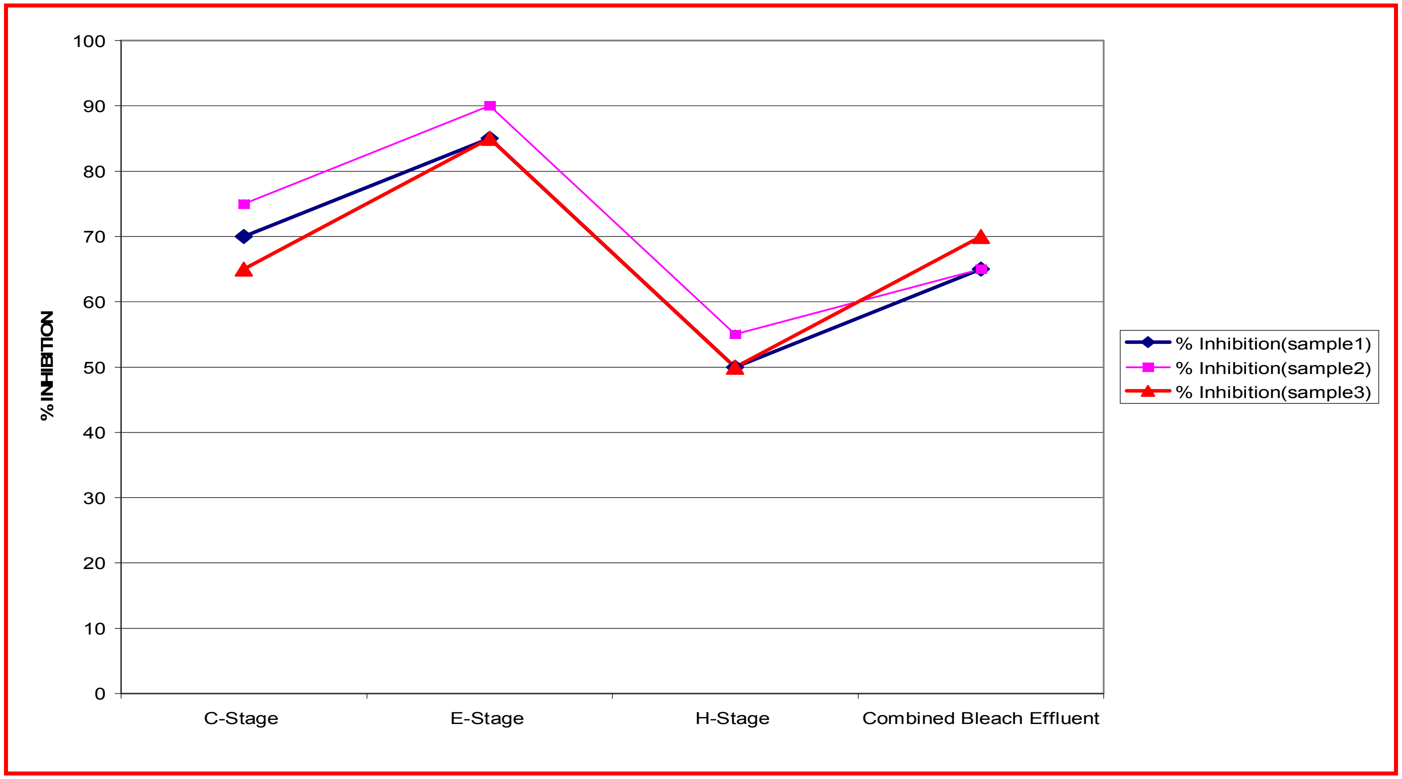

Fig 4.12 - % Inhibition of Luminescent Bacteria Bleach Effluents of Wood Based Mill

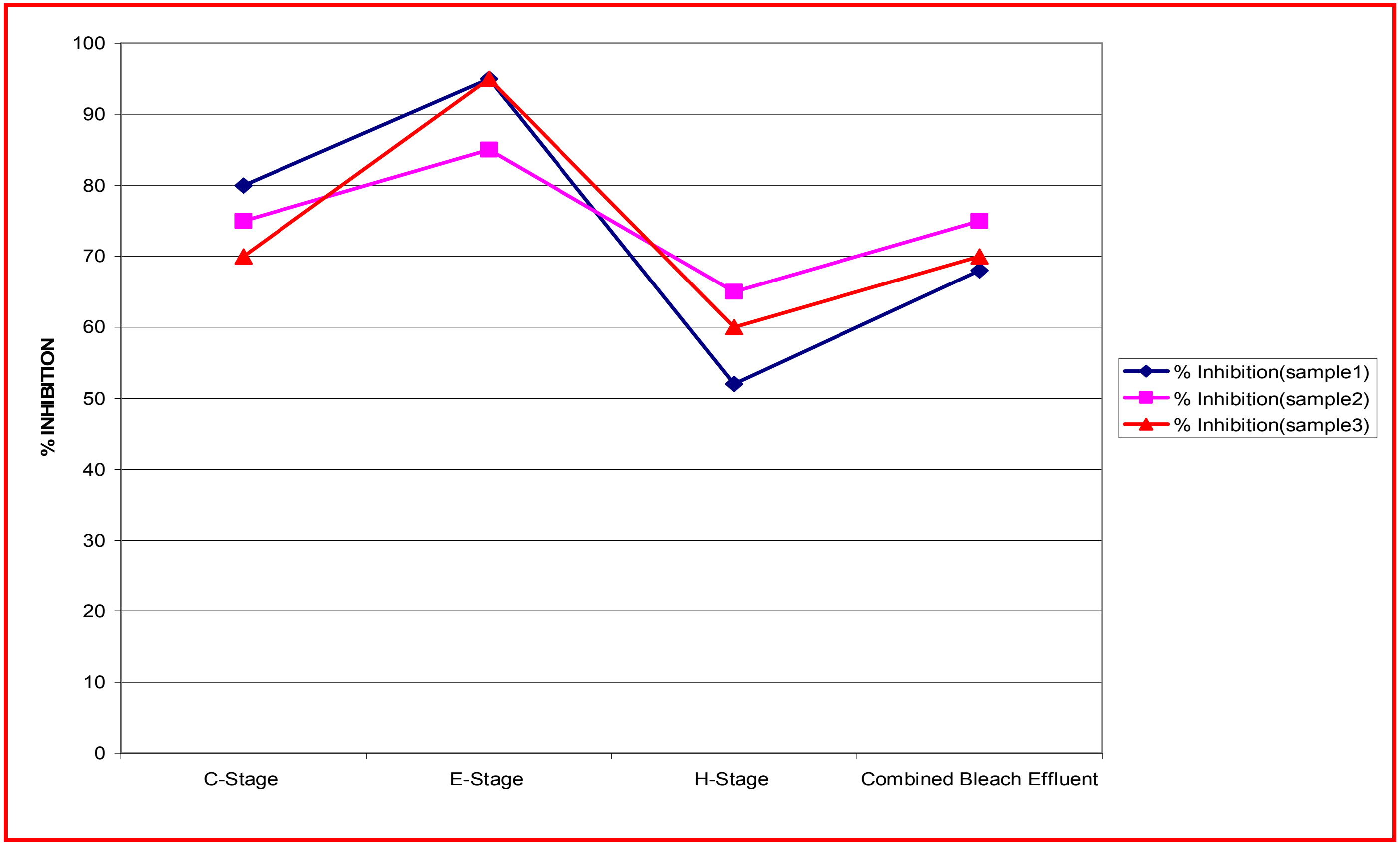

Fig 4.13 - % Inhibition of Luminescent Bacteria Bleach Effluents of Agro Based Mill

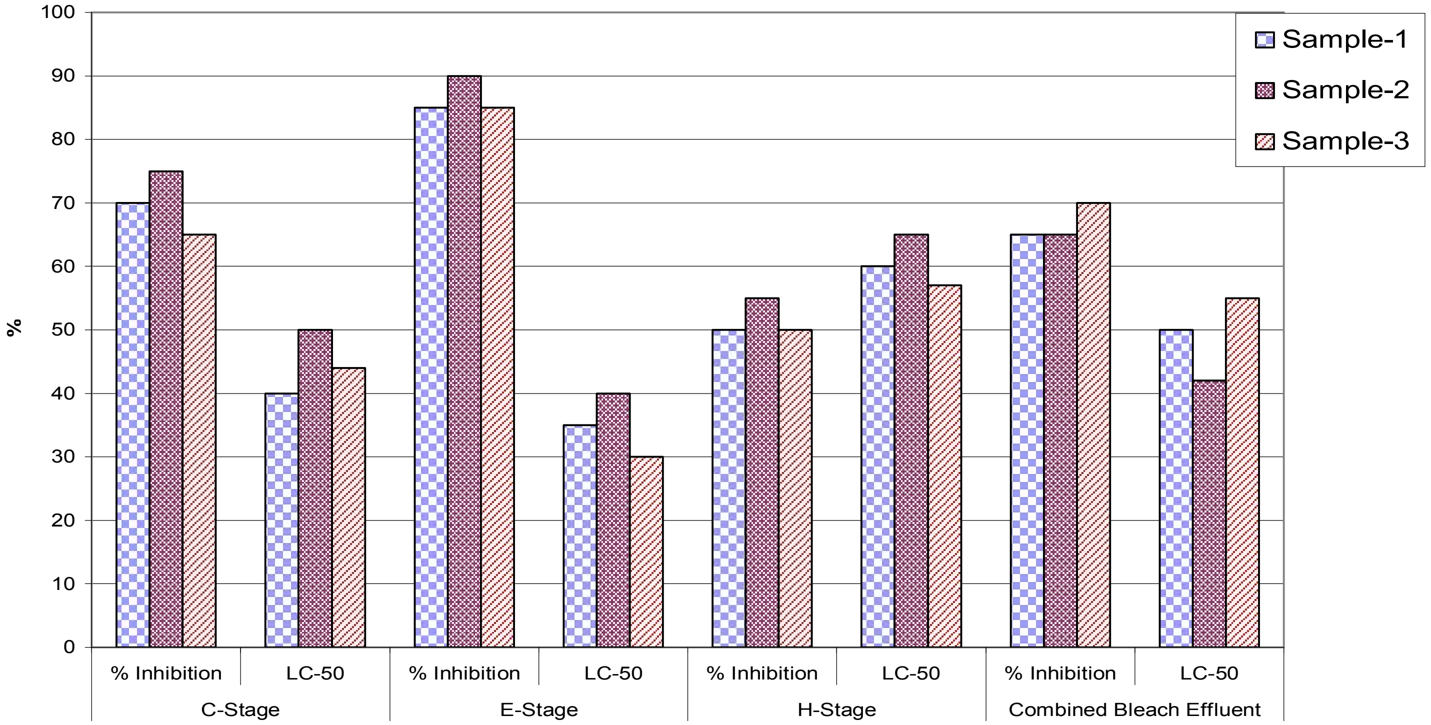

Fig 4.14 - % Inhibition of Luminescent Bacteria and LC_{50} of Bleach Effluents of Wood Based Mill

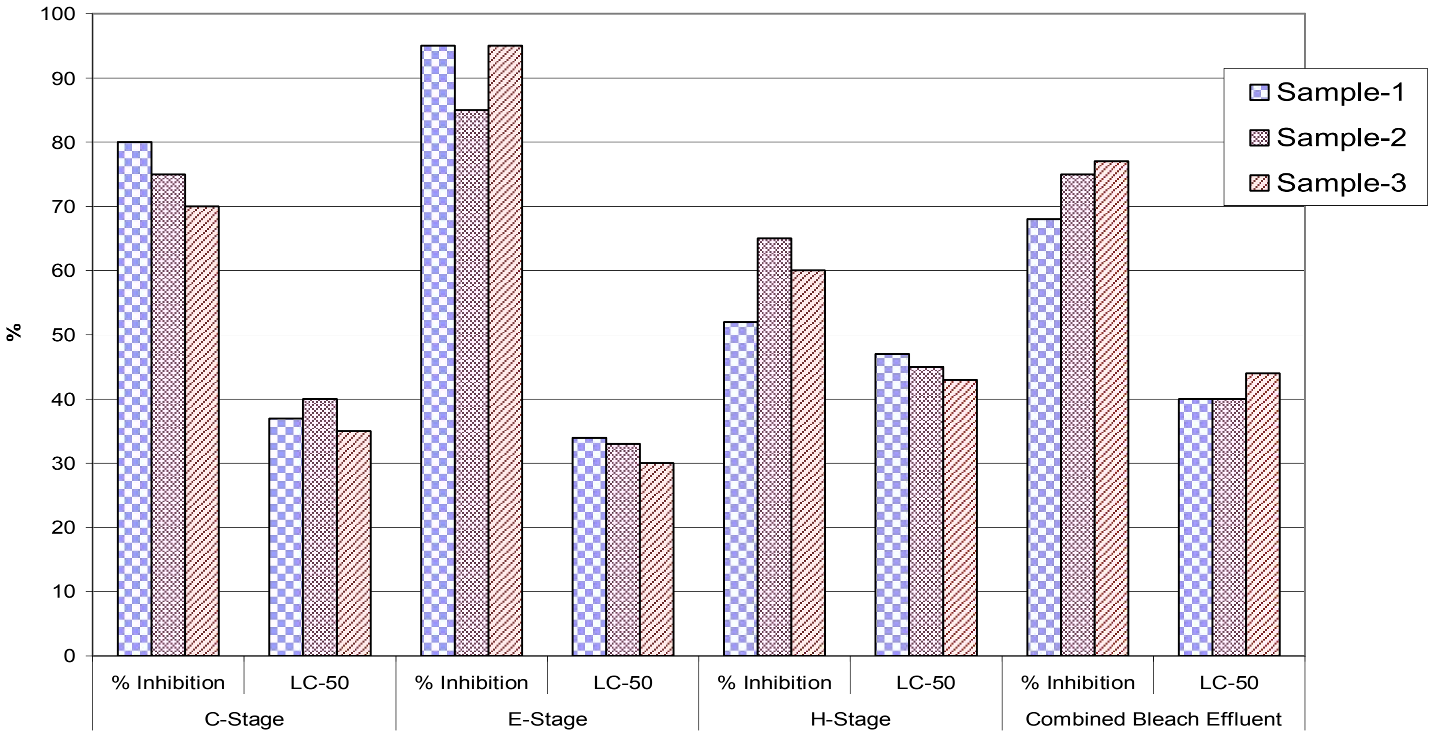

Fig 4.15 - % Inhibition of Luminescent Bacteria and LC_{50} of Bleach Effluents of Agro Based Mill

CHAPTER – 5.0

CONTROL MEASURES FOR REDUCTION OF AOX

Since adoption of modern fiber line technologies in Indian Pulp & Paper Mills is difficult due to raw material, scale of operation, capital investment constraints, so the following studies have been focused on at source and end of pipe treatment option for reducing and controlling the level of AOX in pulp and paper mill effluents.

In this chapter, the different control measures for reduction of AOX through physico – chemical treatment methods are discussed.

5.1 CHEMICAL TREATMENT STUDIES-

The studies were focused mainly on:

- Collection of bleach plant and combined mill effluent samples from wood based and agro based mills producing writing and printing grade of paper.
- Optimization of the chemical dosages.
- Optimization treatment conditions.
- Evaluation of efficiency of combination of chemicals to reduce the level of toxic material in bleach plant effluent.

The lime, alum (Aluminum sulfate) ($Al_2(SO_4)_3$) , and polymer (PAA) chemicals commonly available in paper industry were evaluated for their efficiency in reducing Adsorbable Organic Halide (AOX). The experimental procedure followed was as under :

- For each chemical treatment, 100 ml of effluent sample were taken in the beaker. The alum and lime (procured from the mill) were added and stirred for five minutes. The dosage of chemical for the treatment was fixed on the basis of COD of the effluent.

- The dosage of chemicals was optimized based on reduction in AOX achieved.

- Polymer was used for the better settleabilty of the precipitated sludge formed during the chemical treatment.

- Impact of chemical treatment on toxicity level of bleach plant effluent was also studied using microtox toxicity analyzer.

The response of chemicals used for treatment of bleach plant effluent collected from agro based mill are tabulated in **Table–5.1, 5.2 & 5.3** and depicted in **Fig - 5.2-5.4 & 5.8, 5.9.** And chemical treatment of bleach effluents collected from wood based mill are given in **Table – 5.4, 5.5 & 5.6** and **Fig – 5.5-5.7 & 5.10, 5.11.**

TABLE-5.1

CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(AGRO BASED MILL)
(SAMPLE-1)

Parameters	**C-stage effluent**	**E-stage effluent**	**Combined bleach plant effluent**
(A) Effluent Characteristics			
Sample taken, ml	**100**	**100**	**100**
pH	**2.5**	**7.1**	**6.6**
COD, mg/l	**880**	**1912**	**1802**
AOX, mg/l	**70.4**	**99.2**	**75.0**
Color, PCU	**337**	**3778**	**2689**
(B) Chemical Dosages			
Alum : COD	**1:1**	**0.5:1**	**1:1**
Lime : COD	**1.5 : 1**	**0.5:1**	**1.5:1**
PAA, ml/l (1% solution)	**1.0**	**2.0**	**2.0**
(C) Chemical Treated Effluent Characteristics			
pH	5.5	5.6	5.6
COD, mg/l	282	438	542
AOX, mg/l	**34.5**	**42.5**	**33.6**
Color, PCU	75	512	510
(D) Reduction Efficiency, %			
COD	68	77	71
AOX	**51**	**57.2**	**55.2**
Color	78	86	81

TABLE-5.2

CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(AGRO BASED MILL)
(SAMPLE-2)

Parameters	**C-stage effluent**	**E-stage effluent**	**Combined bleach plant effluent**
(A) Effluent Characteristics			
Sample taken, ml	**100**	**100**	**100**
pH	**2.0**	**9.5**	**5.8**
COD, mg/l	**990**	**1452**	**1420**
AOX, mg/l	**72**	**92**	**54**
Color, PCU	**340**	**3818**	**1402**
(B) Chemical Dosages			
Alum : COD	**1:1**	**0.5:1**	**1:1**
Lime : COD	**1.5 : 1**	**0.5:1**	**1.5:1**
PAA, ml/l (1% solution)	**1.0**	**2.0**	**2.0**
(C) Chemical Treated Effluent Characteristics			
pH	5.8	5.9	**6**.6
COD, mg/l	300	422	554
AOX, mg/l	**32.4**	**44.2**	**23.2**
Color, PCU	70	525	411
(D) Reduction Efficiency, %			
COD	70	71	61
AOX	**55**	**52**	**57**
Color	79	86	71

TABLE-5.3

CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(AGRO BASED MILL)
(SAMPLE-3)

Parameters	**C-stage effluent**	**E-stage effluent**	**Combined bleach plant effluent**
(A) Effluent Characteristics			
Sample taken, ml	**100**	**100**	**100**
pH	**1.8**	**9.1**	**6.9**
COD, mg/l	**980**	**2250**	**1600**
AOX, mg/l	**73**	**108.3**	**60**
Color, PCU	**400**	**4200**	**1250**
(B) Chemical Dosages			
Alum : COD	**1:1**	**0.5:1**	**1:1**
Lime : COD	**1.5 : 1**	**0.5:1**	**1.5:1**
PAA, ml/l (1% solution)	**1.0**	**2.0**	**2.0**
(C) Chemical Treated Effluent Characteristics			
pH	5.2	6.3	7.2
COD, mg/l	282	880	520
AOX, mg/l	**32.0**	**42.0**	**25.5**
Color, PCU	55	468	220
(D) Reduction Efficiency, %			
COD	71	61	68
AOX	**56**	**61**	**58**
Color	86	89	82

TABLE-5.4

CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(WOOD BASED MILL)
(SAMPLE-1)

Parameters	**C-stage effluent**	**E-stage effluent**	**Combined bleach plant effluent**
(A) Effluent Characteristics			
Sample taken, ml	**100**	**100**	**100**
pH	**2.0**	**9.0**	**6.4**
COD, mg/l	**851**	**1818**	**1361**
AOX, mg/l	**54.2**	**92.0**	**45.8**
Color, PCU	**392**	**3692**	**1048**
(B) Chemical Dosages			
Alum : COD	**1:1**	**0.5:1**	**1:1**
Lime : COD	**0.75 : 1**	**0.5:1**	**1:1**
PAA, ml/l (1% solution)	**1.0**	**1.0**	**1.0**
(C) Chemical Treated Effluent Characteristics			
pH	5.5	5.7	5.6
COD, mg/l	240	526	366
AOX, mg/l	**20.2**	**28.5**	**16.2**
Color, PCU	67.0	393	61.0
(D) Reduction Efficiency, %			
COD	72	71	73
AOX	**63**	**69**	**65**
Color	83	89	94

TABLE-5.5

CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT (WOOD BASED MILL)

(SAMPLE-2)

Parameters	**C-stage effluent**	**E-stage effluent**	**Combined bleach plant effluent**
(A) Effluent Characteristics			
Sample taken, ml	**100**	**100**	**100**
pH	**2.3**	**9.8**	**6.4**
COD, mg/l	**912**	**1620**	**1398**
AOX, mg/l	**42**	**92**	**50**
Color, PCU	**364**	**3456**	**1542**
(B) Chemical Dosages			
Alum : COD	**1:1**	**0.5:1**	**1:1**
Lime : COD	**0.75 : 1**	**0.5:1**	**1:1**
PAA, ml/l (1% solution)	**1.0**	**1.0**	**1.0**
(C) Chemical Treated Effluent Characteristics			
pH	**5**.9	6.2	6.0
COD, mg/l	222	422	445
AOX, mg/l	**19.2**	**40.3**	**12.5**
Color, PCU	60	490	89
(D) Reduction Efficiency, %			
COD	76	74	68
AOX	**54**	**56**	**60**
Color	84	86	94

TABLE-5.6

CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(WOOD BASED MILL)
(SAMPLE-3)

Parameters	**C-stage effluent**	**E-stage effluent**	**Combined bleach plant effluent**
(A) Effluent Characteristics			
Sample taken, ml	**100**	**100**	**100**
pH	**2.8**	**9.5**	**6.2**
COD, mg/l	**1240**	**2524**	**1262**
AOX, mg/l	**50.5**	**79.5**	**54.5**
Color, PCU	**364**	**3440**	**2542**
(B) Chemical Dosages			
Alum : COD	**1:1**	**0.5:1**	**1:1**
Lime : COD	**0.75 : 1**	**0.5:1**	**1:1**
PAA, ml/l (1% solution)	**1.0**	**1.0**	**1.0**
(C) Chemical Treated Effluent Characteristics			
pH	5.9	6.2	6.0
COD, mg/l	255	410	300
AOX, mg/l	**25.1**	**32.6**	**25.2**
Color, PCU	66	920	295
(D) Reduction Efficiency, %			
COD	79	84	76
AOX	**50**	**49**	**54**
Color	82	73	88

TABLE-5.7

MICROTOX TOXICITY OF COMBINED BLEACH PLANT EFFLUENT AFTER CHEMICAL TREATMENT

	% Inhibition, Agro Based Mill		**% Inhibition , Wood Based Mill**	
	As such	**After Chemical Treatment**	**As such**	**After Chemical Treatment**
Sample -1	68	32	65	27
Sample-2	75	38	65	25
Sample-3	70	37	70	30

TABLE-5.8

MICROTOX TOXICITY OF E- STAGE EFFLUENT AFTER CHEMICAL TREATMENT

	% Inhibition, Agro Based Mill		**% Inhibition , Wood Based Mill**	
	As such	**After Chemical Treatment**	**As such**	**After Chemical Treatment**
Sample -1	95	43	85	38
Sample-2	85	40	90	37
Sample-3	95	41	85	37

5.2 PHYSICAL TREATMENT METHODS

5.2.1 CARBON ADSORPTION

Adsorption in general, is the process of collecting soluble substances that are in solution on a suitable interface. The interface can be between the liquid and a gas, a solid or another liquid.

The adsorption process take place in three steps Macrotransport, Microtransport and sorption.

- Macrotransport involves the movement of the material through the water to the liquid solid interface.
- Microtransport involves the diffusion of the organic material through the macropore system of granular activated carbon.
- Adsorption occurs on the surface of the granules.

In these studies bleach plant effluent collected from wood based mills & agro based mill were passed through a column filled with granular activated carbon. The studies were aimed to evaluate the adsorption efficiency as well as the saturation point of activated carbon in order to achieve maximum removal of AOX and also color & COD. A known amount of bleach effluent was passed through the carbon bed and elutes were collected in batches. The treated sample of each batches were analyzed for AOX , COD and Color reduction. The results obtained are shown in **Table- 5.9, 5.10 & 5.11 Fig- 5.13 to 5.20.**

TABLE – 5.9

TREATMENT OF COMBINED BLEACH PLANT EFFLUENT WITH ACTIVATED CARBON (AGRO BASED MILL)

Parameter	**Sample as such**	**1st cycle**	**% Reduction**	**2nd cycle**	**% Reduction**
COD, mg/l	1880	540	71	700	62
T.S., mg/l	4420	3100	30	3480	21
TDS, mg/l	4050	3044	25	3840	18
Color, PCU	4958	1000	80	1690	66
AOX, mg/l	**102**	**22**	**78**	**30**	**71**

Parameter	**3rd cycle**	**% Reduction**	**4th cycle**	**% Reduction**	**5th cycle**	**% Reduction**
COD, mg/l	880	53	940	50	1312	30
T.S., mg/l	3785	14	3850	13	3950	11
TDS, mg/l	3600	11	3740	8	3888	4
Color, PCU	2860	42	3580	28	3670	26
AOX, mg/l	**40**	**61**	**48**	**53**	**77.5**	**24**

TABLE-5.10

TREATMENT OF COMBINED BLEACH PLANT EFFLUENT WITH ACTIVATED CARBON (WOOD BASED MILL)

Sample -1

Parameter	**Sample as such**	**1st cycle**	**% Reduction**	**2nd cycle**	**% Reduction**
COD, mg/l	1278	421	67	512	60
T.S., mg/l	3105	2011	35	2402	23
TDS, mg/l	2515	2015	20	2102	16
Color , PCU	1412	275	81	514	64
AOX, mg/l	**62.3**	**15.9**	**74**	**18.5**	**70**

Parameter	**3rd cycle**	**% Reduction**	**4th cycle**	**% Reduction**	**5th cycle**	**% Reduction**
COD, mg/l	617	52	715	44	914	28
T.S., mg/l	2578	17	2657	14	2816	9
TDS, mg/l	2182	13	2253	10	2475	2
Color , PCU	715	49	975	31	1102	22
AOX, mg/l	**26.7**	**57**	**38.2**	**39**	**45.2**	**27**

TABLE-5.11

TREATMENT OF COMBINED BLEACH PLANT EFFLUENT WITH ACTIVATED CARBON (WOOD BASED MILL)

SAMPLE -2

Parameter	**Sample as such**	**1st cycle**	**% Reduction**	**2nd cycle**	**% Reduction**
COD, mg/l	1315	405	69	517	61
T.S., mg/l	2485	1552	38	1852	25
TDS, mg/l	1675	1359	19	1416	15
Color , PCU	1372	270	80	455	67
AOX, mg/l	**57.2**	**15.6**	**73**	**17.5**	**69**

Parameter	**3rd cycle**	**% Reduction**	**4th cycle**	**% Reduction**	**5th cycle**	**% Reduction**
COD, mg/l	653	50	717	45	916	30
T.S., mg/l	2013	19	2200	11	2321	7
TDS, mg/l	1452	13	1523	9	1601	4
Color, PCU	658	52	859	37	1025	25
AOX, mg/l	**26.8**	**53**	**33.5**	**41**	**40.2**	**30**

5.2.2 THERMAL TREATMENT:

In other studies the effect of heat treatment are also carried out to evaluate the effect of heat treatment on volatility of AOX in bleach filtrate collected from wood based mill and agro based mill. The results obtained are shown in **Table 5.12 to 5.14 and Figs. 5.21 & 5.22.** It has been observed that the reduction in AOX in C-stage effluent at 50°C and 80°C was 12.5-23% and 27-29% respectively. The reduction in color and COD were not found.

TABLE-5.12

THERMAL TREATMENT OF BLEACH PLANT EFFLUENT

(WOOD BASED MILL)

SAMPLE – 1

S.No.	Samples	AOX, mg/l As such	Thermal Treatment			
			50°C		80°C	
			AOX, mg/l	% Reduction	AOX, mg/l	% Reduction
1.	C-Stage	48.9	38.5	21	35.5	27.5
2.	E-Stage	80.4	64.8	19.5	56.2	30
3.	Combined bleach effluent	50.2	39.7	21	36.2	28

TABLE-5.13
THERMAL TREATMENT OF BLEACH PLANT EFFLUENT
(WOOD BASED MILL)
SAMPLE – 2

S.No.	Samples	AOX, mg/l As such	Thermal Treatment			
			50°C		80°C	
			AOX, mg/l	% Reduction	AOX, mg/l	% Reduction
1.	C-Stage	45.6	35.2	23	33.2	27
2.	E-Stage	85.2	65.2	23.5	59.2	31
3.	Combined bleach effluent	52.3	40.2	24	36.2	31

TABLE-5.14
THERMAL TREATMENT OF BLEACH PLANT EFFLUENT
(AGRO BASED MILL)
SAMPLE – 3

S.No.	Samples	AOX, mg/l As such	Thermal Treatment			
			50°C		80°C	
			AOX, mg/l	% Reduction	AOX, mg/l	% Reduction
1.	C-Stage	60.5	52.9	12.5	42.6	29
2.	E-Stage	99.5	80.5	19	60.5	30
3.	Combined Bleach Effluent	59.3	48.5	18	43.4	26.8

5.3 BIOLOGICAL TREATMENT TO REDUCE THE AOX

The objective of this study is to evaluate the treatment facility in small scale agro based mill and large scale wood based mill for reduction of AOX. The main treatment system of ETP is Activated sludge process where the reduction of AOX takes place. For this study, ETP inlet samples (influent) and outlet samples (effluent) were collected from both type of wood based mill which are using the lime and alum as chemical treatment prior going to ETP and which are not using the chemical treatment and also from agro based mill with conventional effluent treatment system. Most of the agro based mills are not using the chemical (Lime & Alum) treatment in the effluent treatment plant. The results of ETP inlet and outlet samples collected from the agro and wood based mills are given in the **Table 5.15 to 5.23 and Fig 5.23 to 5.25.**

TABLE-5.15

AOX REDUCTION THROUGH BIOLOGICAL PROCESS (WOOD BASED MILL USING LIME & ALUM)

	Sample -1		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	8.5	7.5	
TSS, mg/l	586	15	97
TDS, mg/l	1056	770	27
COD, mg/l	818	200	75.5
BOD mg/l	320	15	95
Color, PCU	358	238	34
Lignin, mg/l	54	39	27
AOX, mg/l	**22.5**	**7.2**	**68**

Note- Mill was using lime and alum in to the influent at inlet to ETP

TABLE-5.16

AOX REDUCTION THROUGH BIOLOGICAL PROCESS (WOOD BASED MILL USING LIME & ALUM)

	Sample -2		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	8.82	7.56	
TSS, mg/l	1290	32	97
TDS, mg/l	2272	1164	48
COD, mg/l	659	141	78
BOD, mg/l	247	27	89
Color, PCU	333	235	29
Lignin, mg/l	73	45	38
AOX, mg/l	**21.0**	**6.3**	**70**

Note- Mill was using lime and alum in to the influent at inlet to ETP

TABLE-5.17

AOX REDUCTION THROUGH BIOLOGICAL PROCESS
(WOOD BASED MILL USING LIME & ALUM)

	Sample -3		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	9.4	7.61	
TSS, mg/l	1045	40	96
TDS, mg/l	1575	1300	17
COD, mg/l	923	182	80
BOD, mg/l	380	25	93
Color, PCU	375	250	33
Lignin, mg/l	76	40	47
AOX, mg/l	**33.5**	**11.2**	**67**

Note- Mill was using lime and alum in to the influent at inlet to ETP

TABLE-5.18

AOX REDUCTION THROUGH BIOLOGICAL PROCESS (WOOD BASED MILL NOT USING LIME & ALUM)

	Sample -1		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	8.89	7.79	
TSS., mg/l	1012	95	91
TDS, mg/l	1420	1308	8
COD, mg/l	1025	255	75
BOD, mg/l	332	48	85.5
Color, PCU	514	325	37
Lignin, mg/l	142	92	35
AOX, mg/l	**28.5**	**12.5**	**56**

TABLE-5.19

AOX REDUCTION THROUGH BIOLOGICAL PROCESS (WOOD BASED MILL NOT USING LIME & ALUM)

	Sample -2		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	9.12	7.36	
TSS, mg/l	974	112	89
TDS, mg/l	1345	1280	5
COD, mg/l	1120	316	72
BOD, mg/l	421	46	89
Color, PCU	425	312	27
Lignin, mg/l	133	72	46
AOX, mg/l	**25.5**	**12**	**53**

TABLE-5.20

AOX REDUCTION THROUGH BIOLOGICAL PROCESS (WOOD BASED MILL NOT USING LIME & ALUM)

	Sample -3		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	8.22	7.22	
TSS, mg/l	1128	144	87
TDS, mg/l	1411	1350	4
COD, mg/l	1255	385	69
BOD, mg/l	446	45	90
Color, PCU	875	518	41
Lignin, mg/l	212	95	55
AOX, mg/l	**38.2**	**18.7**	**51**

TABLE-5.21

AOX REDUCTION THROUGH BIOLOGICAL TREATMENT PROCESS (AGRO BASED MILL NOT USING LIME & ALUM)

	Sample -1		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	7.9	7.2	
TSS, mg/l	1385	182	87
TDS, mg/l	2254	1898	16
COD, mg/l	2419	940	61
BOD, mg/l	1129	385	66
Color, PCU	3100	1350	56.5
Lignin, mg/l	440	80	81
AOX, mg/l	**40**	**25**	**38**

TABLE-5.22

AOX REDUCTION THROUGH BIOLOGICAL TREATMENT PROCESS (AGRO BASED MILL NOT USING LIME & ALUM)

	Sample -2		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	8.6	7.42	
TSS, mg/l	939	101	89
TDS, mg/l	2197	1213	44
COD, mg/l	2225	823	63
BOD, mg/l	758	301	60
Color, PCU	1930	1450	24
Lignin, mg/l	392	191	51
AOX, mg/l	**24**	**16.8**	**30**

TABLE-5.23

AOX REDUCTION THROUGH BIOLOGICAL TREATMENT PROCESS (AGRO BASED MILL NOT USING LIME & ALUM)

	Sample -3		
	Inlet to ETP	**Outlet to ETP**	**Reduction, %**
pH	8.12	7.68	
TSS, mg/l	1520	150	90
TDS, mg/l	1890	1254	34
COD, mg/l	2693	1050	61
BOD, mg/l	855	250	71
Color, PCU	2151	1490	31
Lignin, mg/l	540	302	44
AOX, mg/l	**28.8**	**18.7**	**35**

5.4 OTHER IN HOUSE OPTIONS TO CONTROL AOX DISCHARGE LEVEL

As there are limitations before the Indian pulp & paper mills in adopting modern fiber line technologies (as discussed in Chapter 2) for reducing AOX level due to reasons mentioned earlier , other options as mentioned under involving better house keeping , process optimisation etc apart from End of Pipe Treatment Methods discussed above can be adopted to reduce the AOX level .

5.4.1 CONTROLLED PULP MILL OPERATION

The AOX level in the effluent using same bleaching sequence with different Kappa no. pulp are given in **Table –5.24 & 5.25 & Fig-5.26 – 5.27.**

TABLE- 5.24

KAPPA NO. V/S AOX LEVEL (WOOD PULP)

Bleaching Sequence – C, E, H

Kappa No.	**AOX Level, Kg./t pulp**		
	Sample - 1	Sample-2	Sample-3
26	5.8	5.5	5.9
24	4.6	4.5	4.6
20	2.8	2.6	2.8

TABLE-5.25

KAPPA NO. V/S AOX LEVEL (AGRO PULP)

Bleaching Sequence – C, E, H

Kappa No.	**AOX Level, Kg./t pulp**		
	Sample - 1	Sample-2	Sample-3
29	6.6	7.8	7.2
25	5.2	5.7	5.9
22	3.8	4.0	4.1

5.4.2 INCREASED USE OF RECYCLED FIBER

One an other option for reduction in AOX level is use of recycle fibre with the agro chemical pulp. AOX were determined in bleach effluent of 100 % of agro pulp, 75-25 and 50 : 50 agro pulp and recycled fiber . The results are given in the **Table- 5.26.**

TABLE-5.26

REDUCTION OF AOX BY USE OF RECYCLE FIBRE

Type of product	**AOX Level, Kg/t pulp**		
	Sample – 1	Sample-2	Sample-3
Agro – Pulp (100%)	6.6	7.8	7.2
Agro – Pulp & RCF (75%+25%)	5.0	5.5	5.3
Agro – Pulp & RCF (50%+50%)	3.5	4.0	3.8

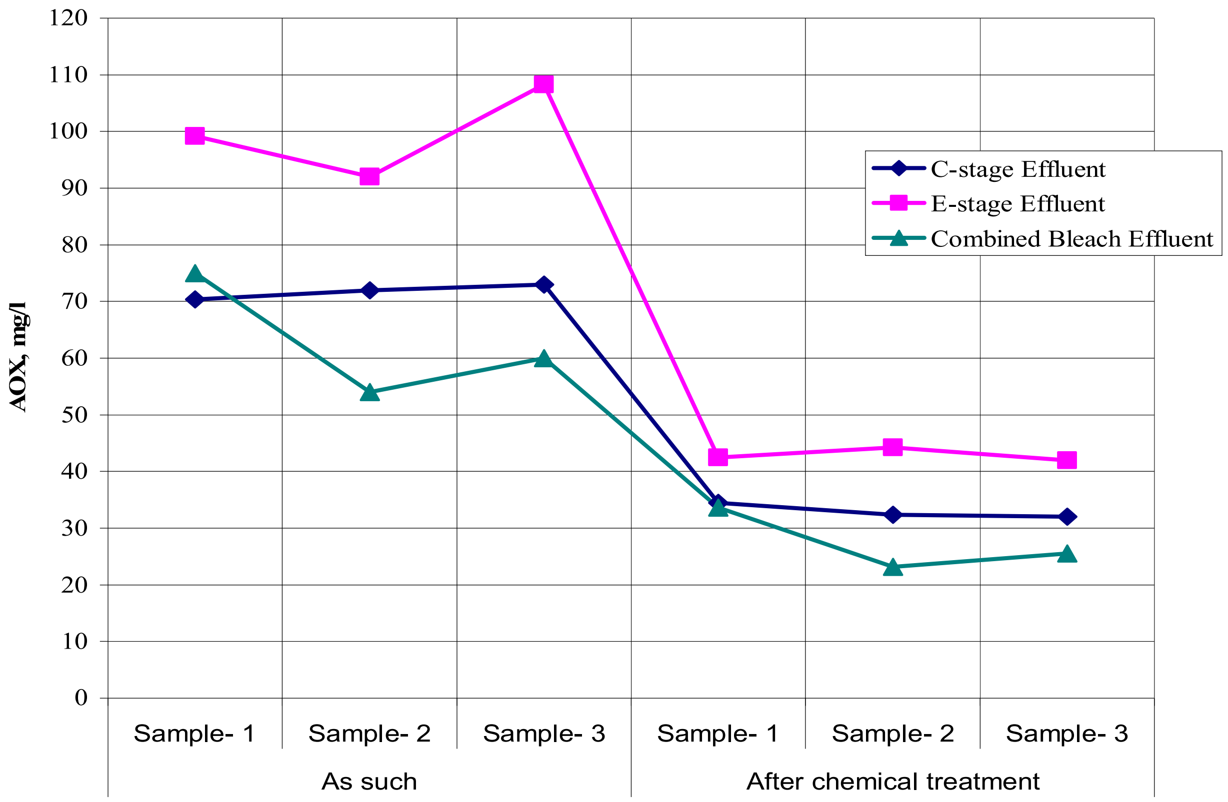

Fig 5.1- Reduction in AOX by Chemical Treatment of Bleach Plant Effluent of Agro Based Mill

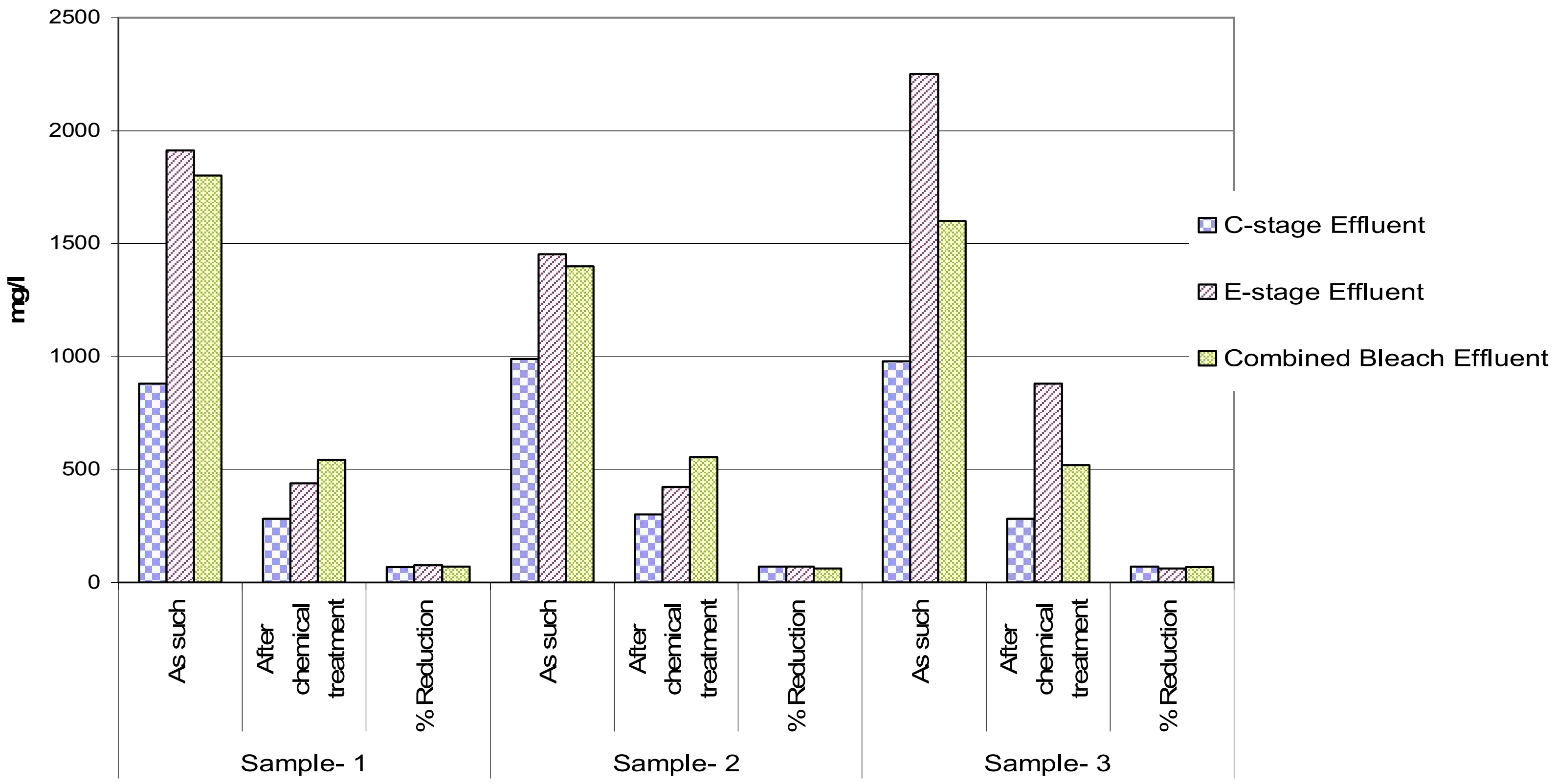

Fig 5.2 - Reduction in COD by Chemical Treatment of Bleach Plant Effluent of Agro Based Mill

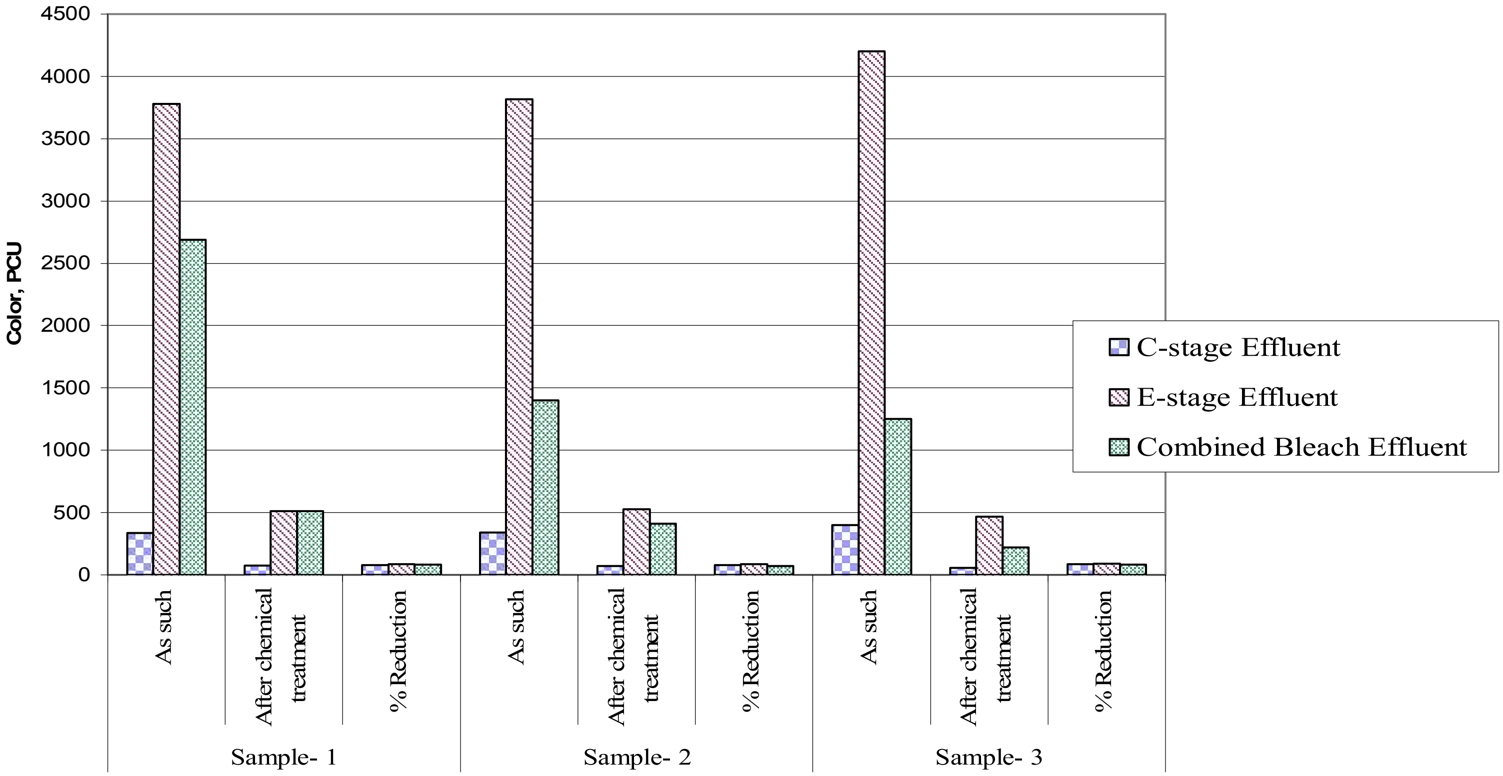

Fig 5.3 - Reduction in Color by Chemical Treatment of Agro Based Mill Bleach Plant Effluent

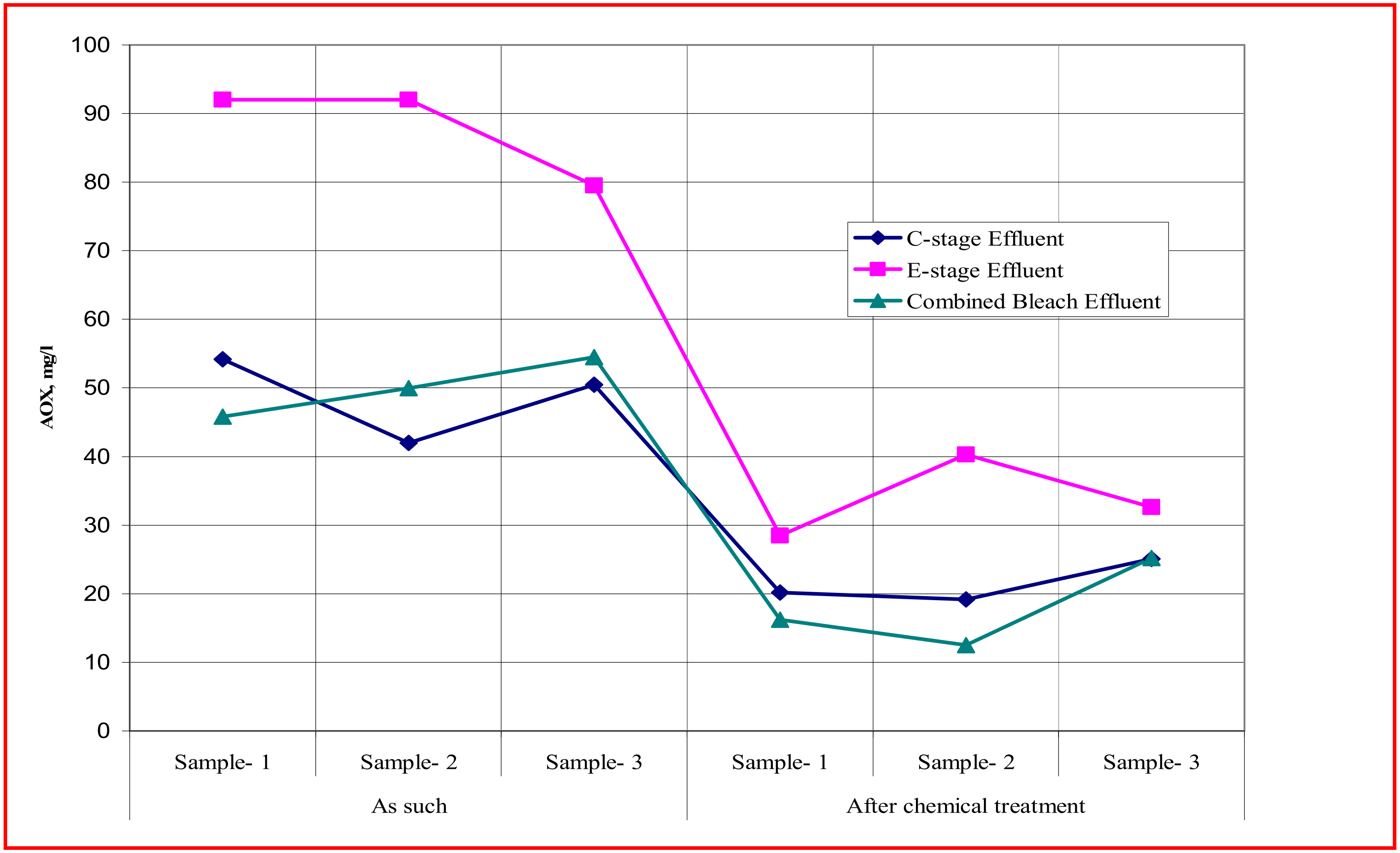

Fig 5.4 - Reduction in AOX by Chemical Treatment of Bleach Plant Effluent of Wood Based Mill

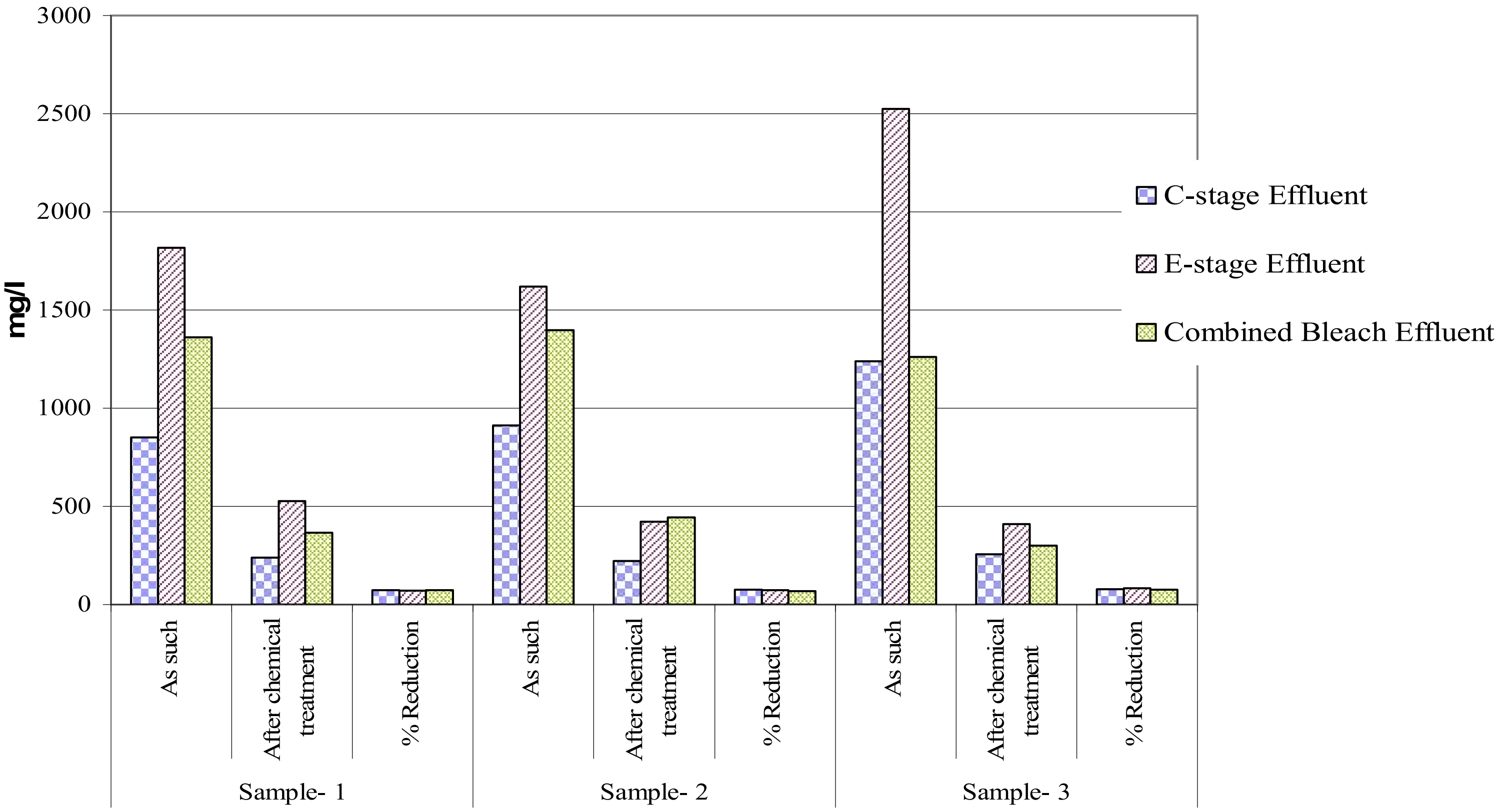

Fig 5.5 - Reduction in COD by Chemical Treatment of Bleach Plant Effluent of Wood Based Mill

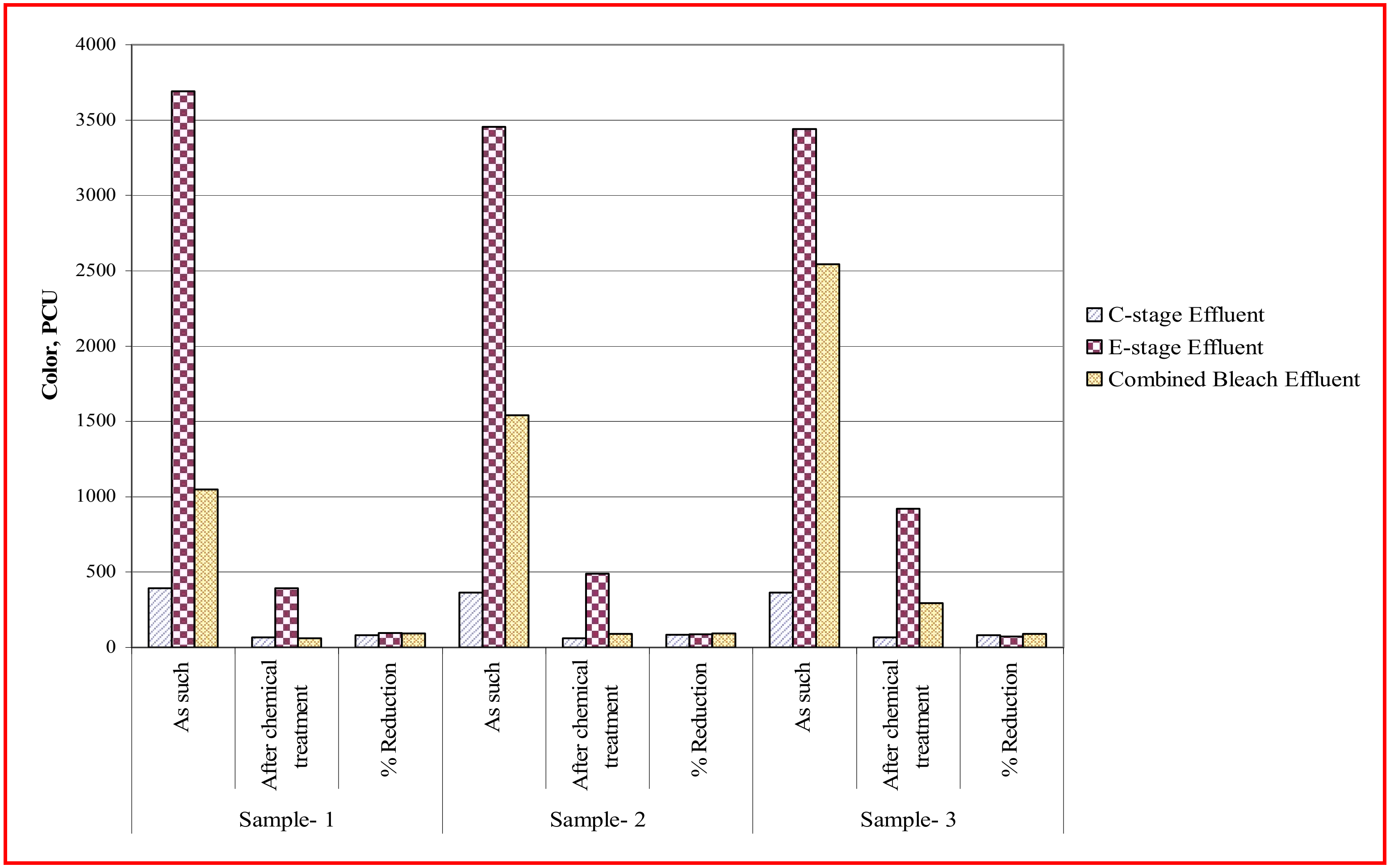

Fig 5.6 - Reduction in Color by Chemical Treatment Bleach Plant Effluent of Wood Based Mill

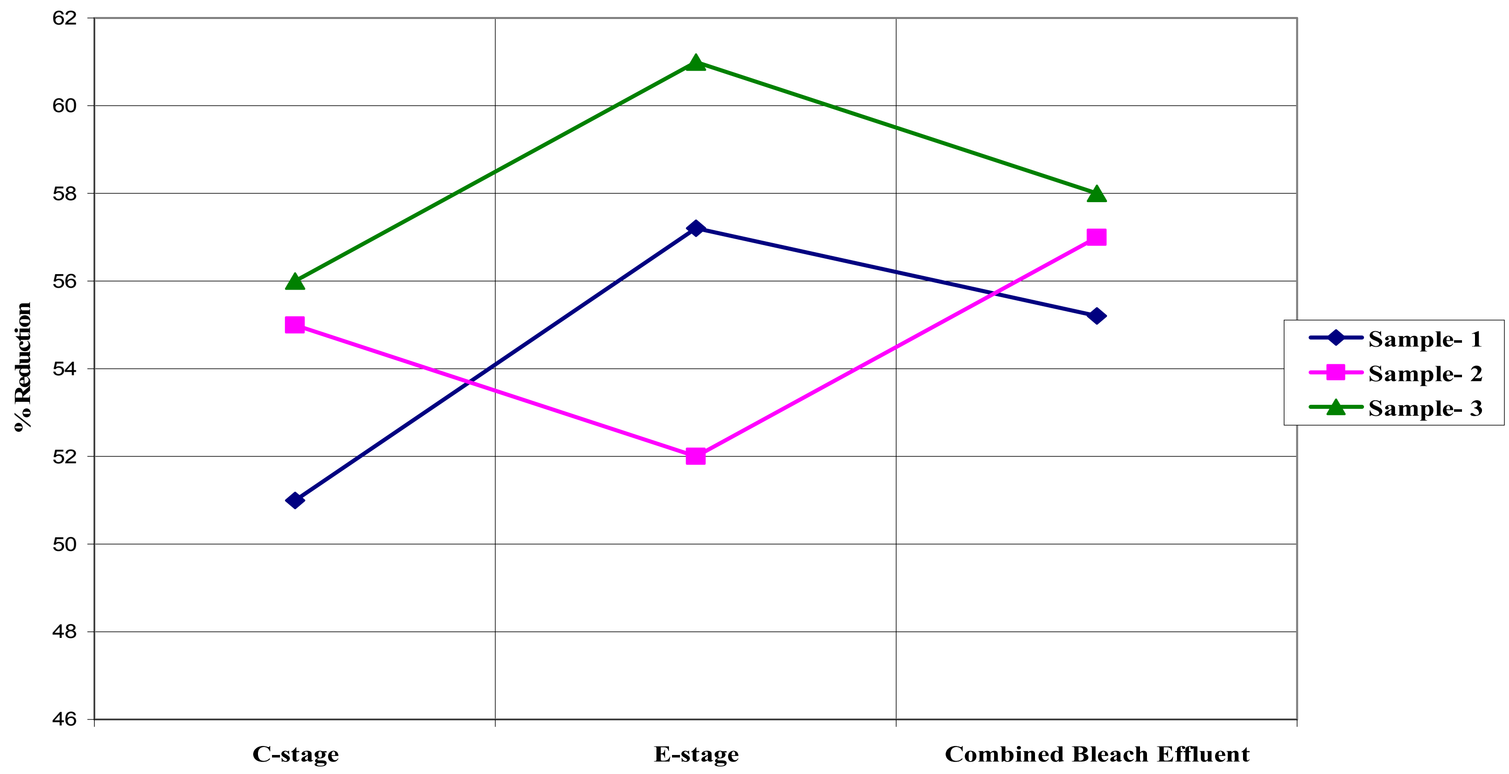

Fig 5.7 - % Reduction in AOX by Chemical Treatment of Bleach Plant Effluent of Agro Based Mill

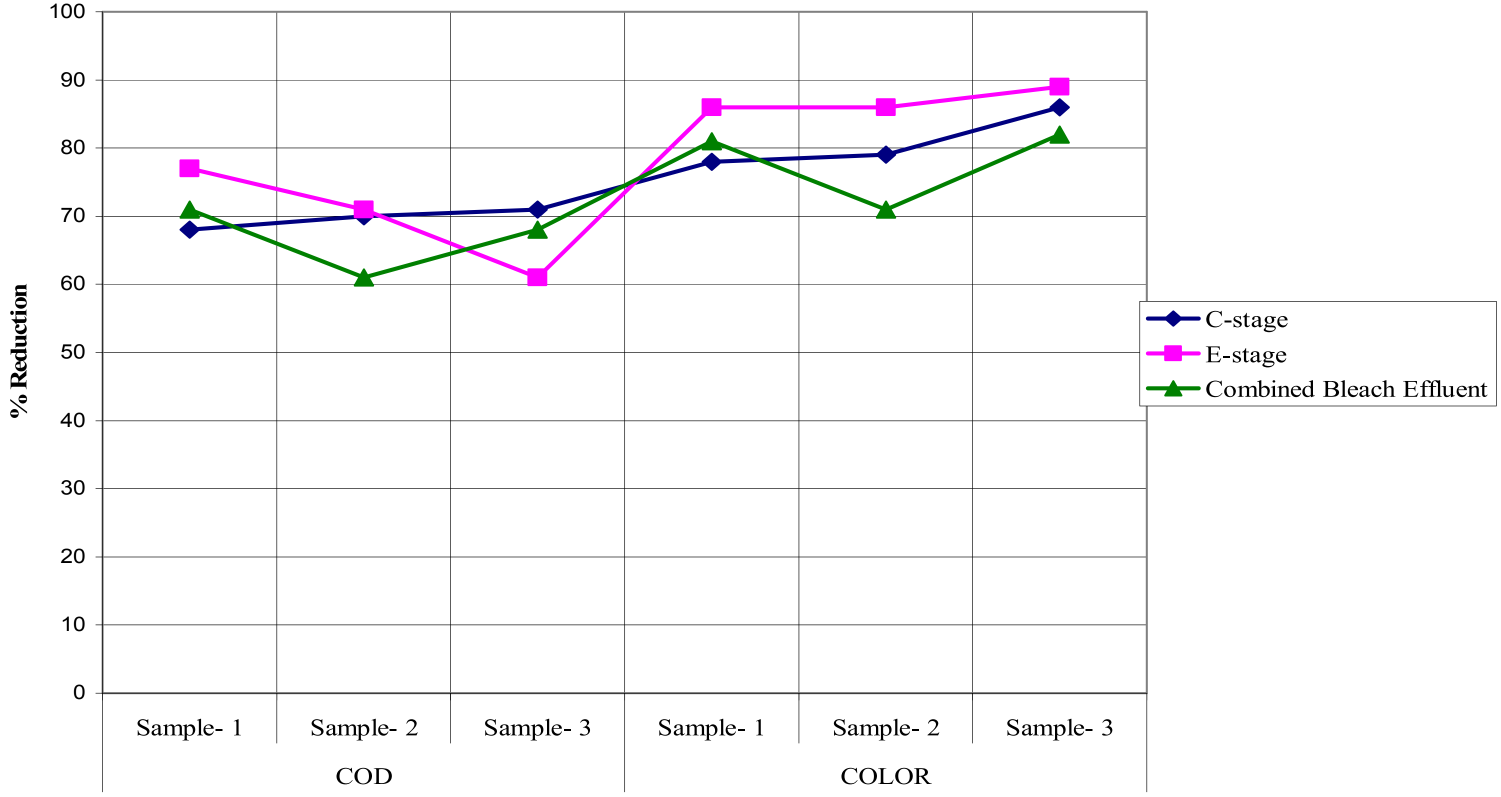

Fig 5.8 - % Reduction in COD & Color by Chemical Treatment of Bleach Plant Effluent of Agro Based Mill)

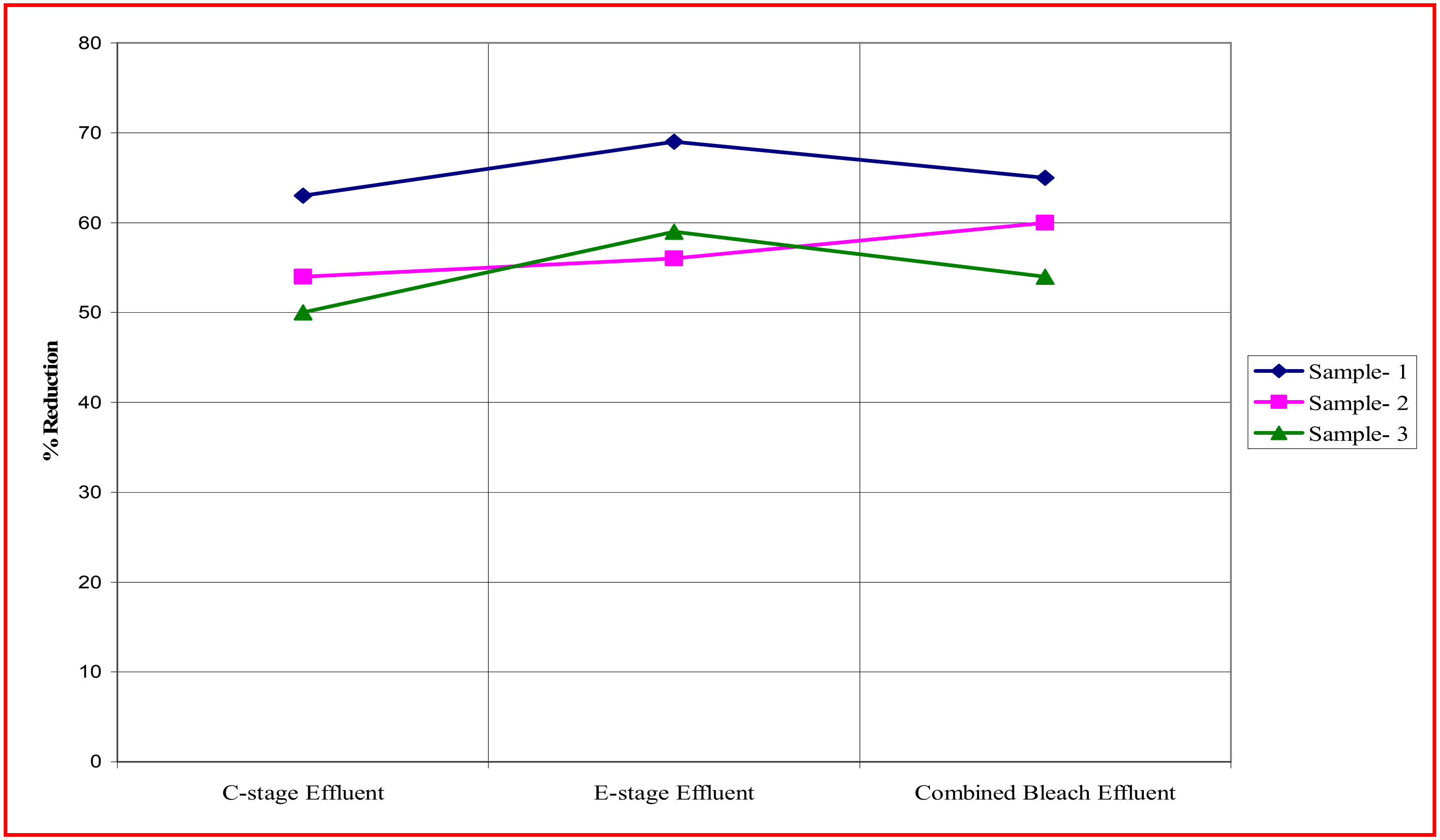

Fig 5.9 - % Reduction in AOX By Chemical Treatment of Bleach Plant Effluent of Wood Based Mill

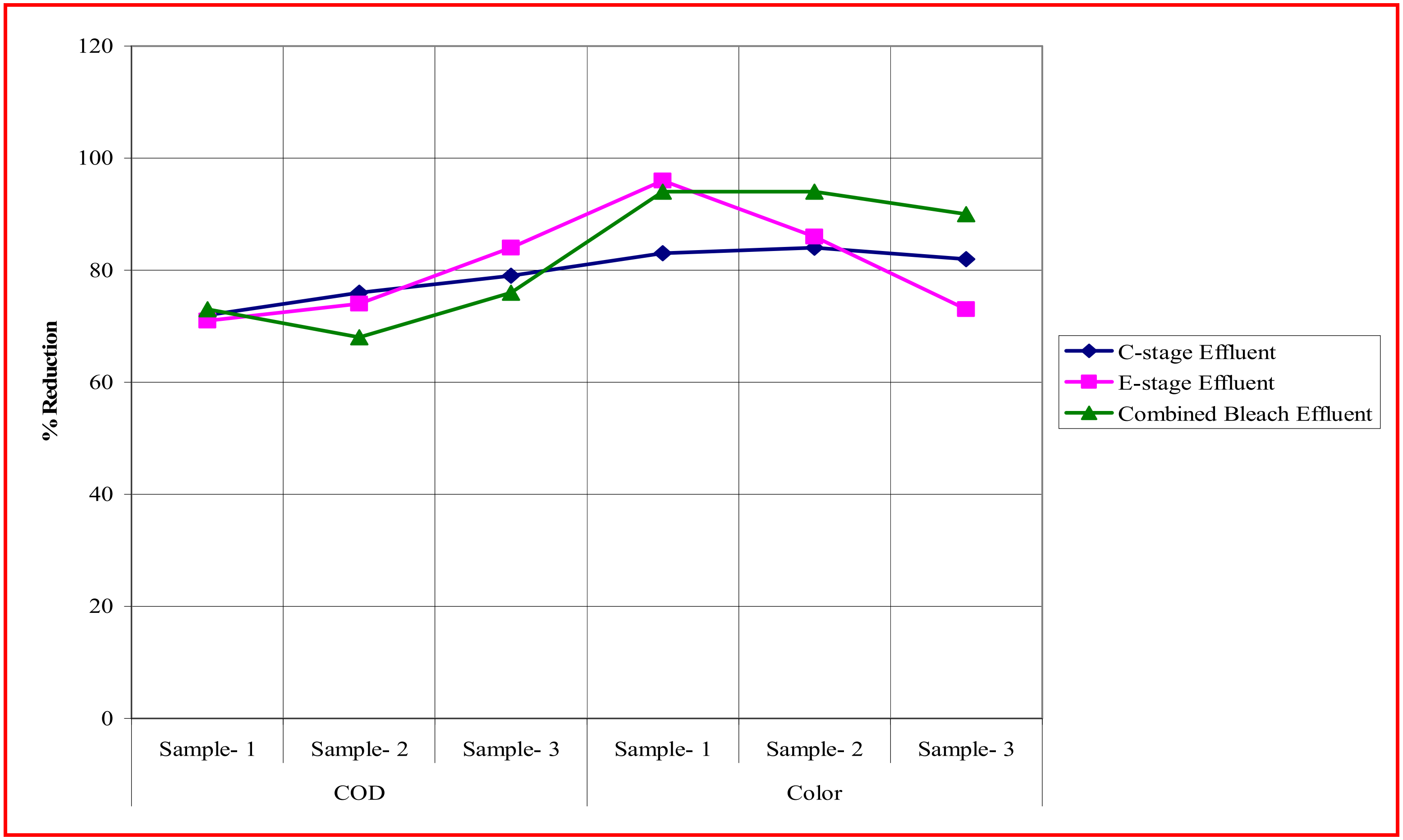

Fig 5.10 - % Reduction in COD & Color by Chemical Treatment of Bleach Plant Effluent of Wood Based Mill

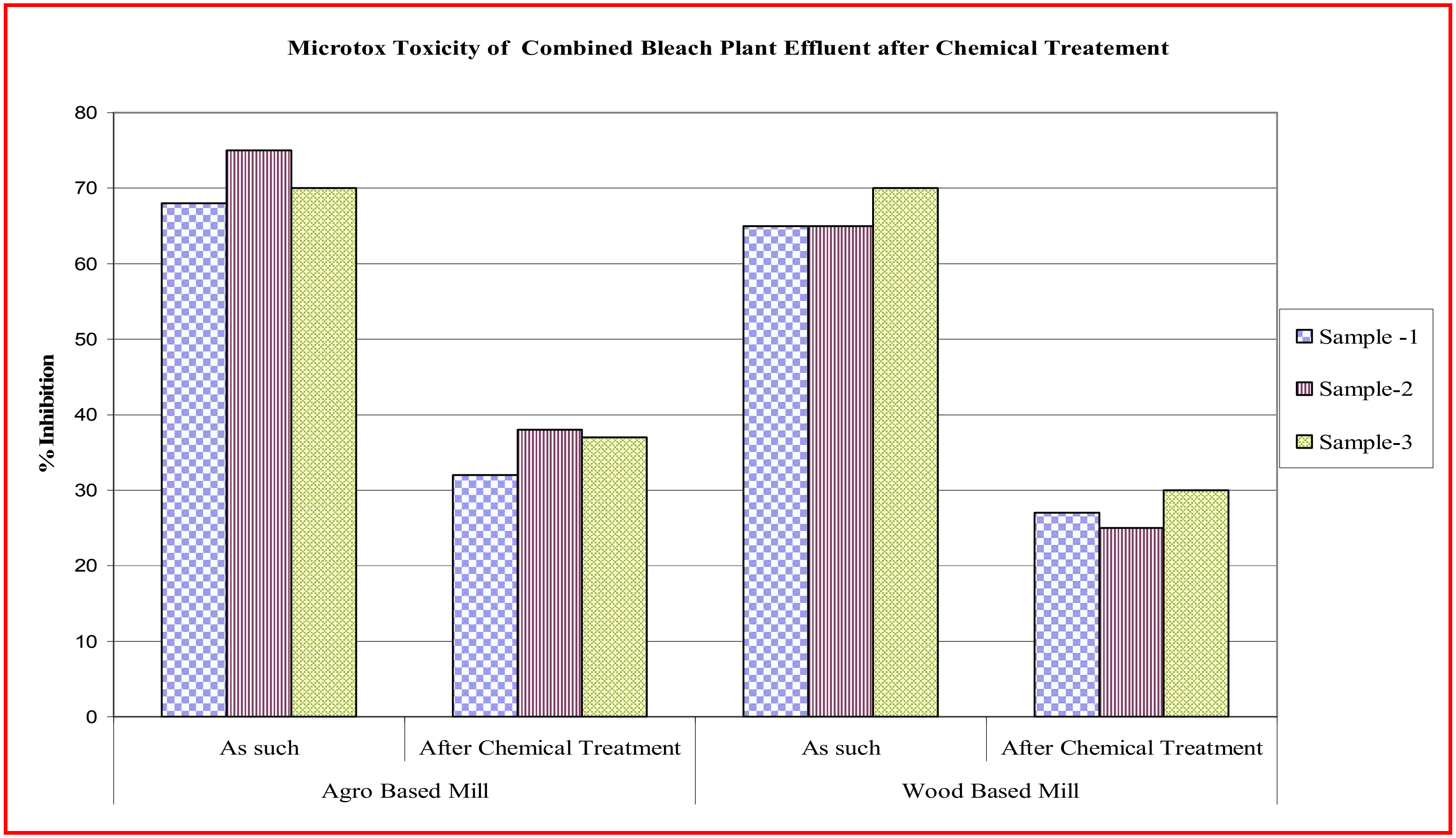

Fig 5.11 - **% Inhibition in Luminescent Bacteria by Combined Bleach Effluent after Chemical Treatment**

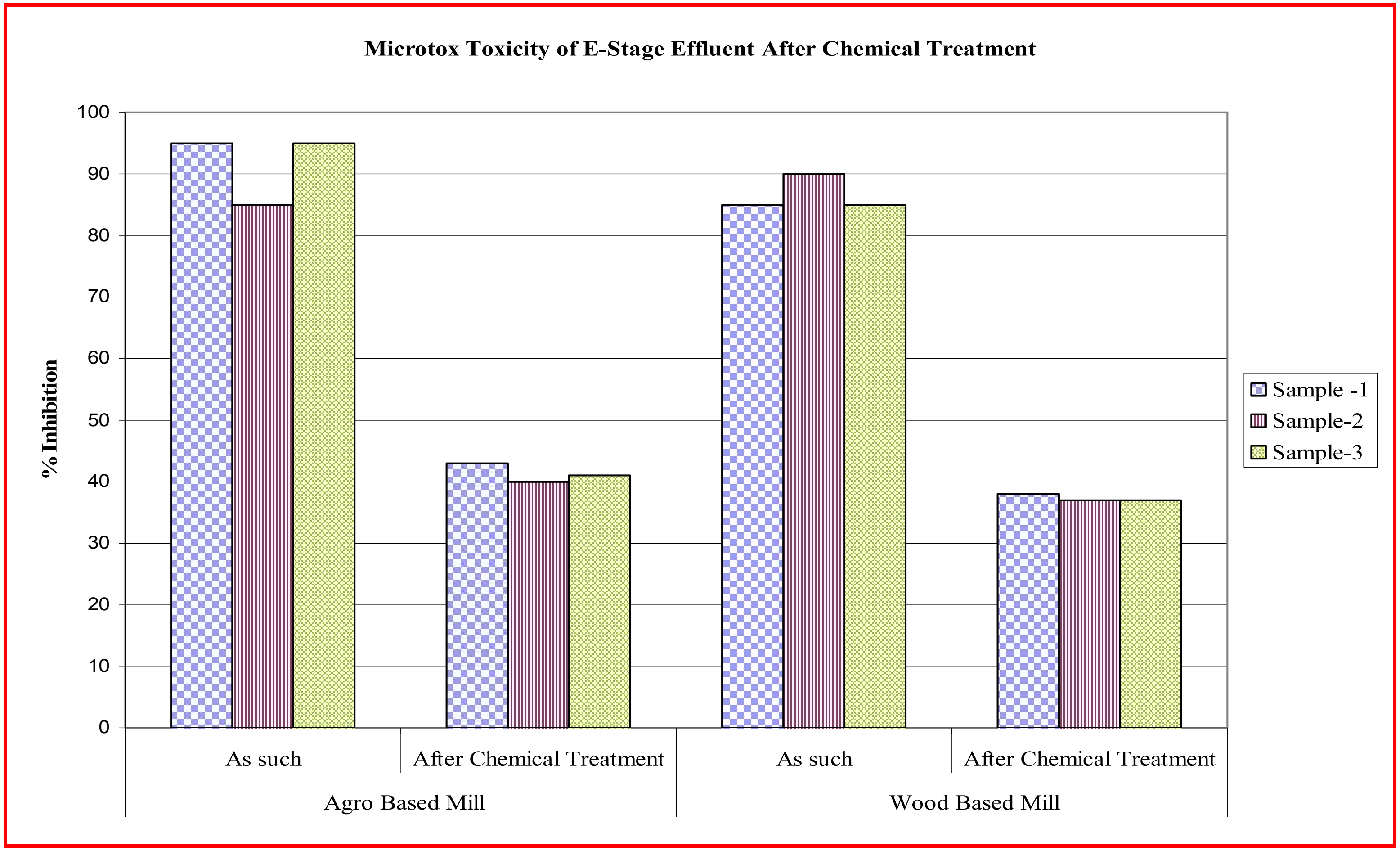

Fig 5.12 - **% Inhibition in Luminescent Bacteria by E-Stage Effluent after Chemical Treatment**

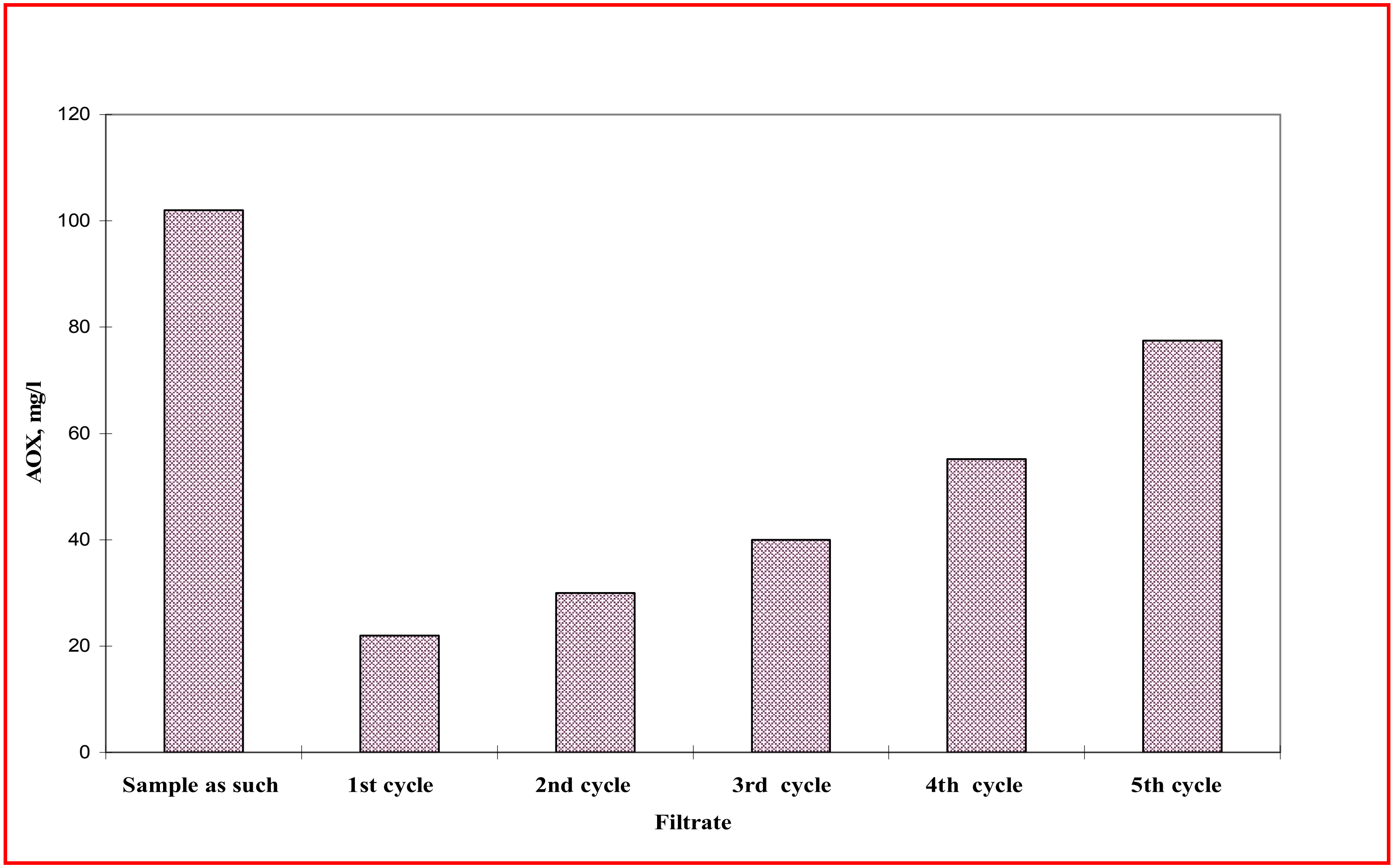

Fig 5.13 - Reduction in AOX level of Bleach Effluent by use of Activated Carbon (Agro Based Mill)

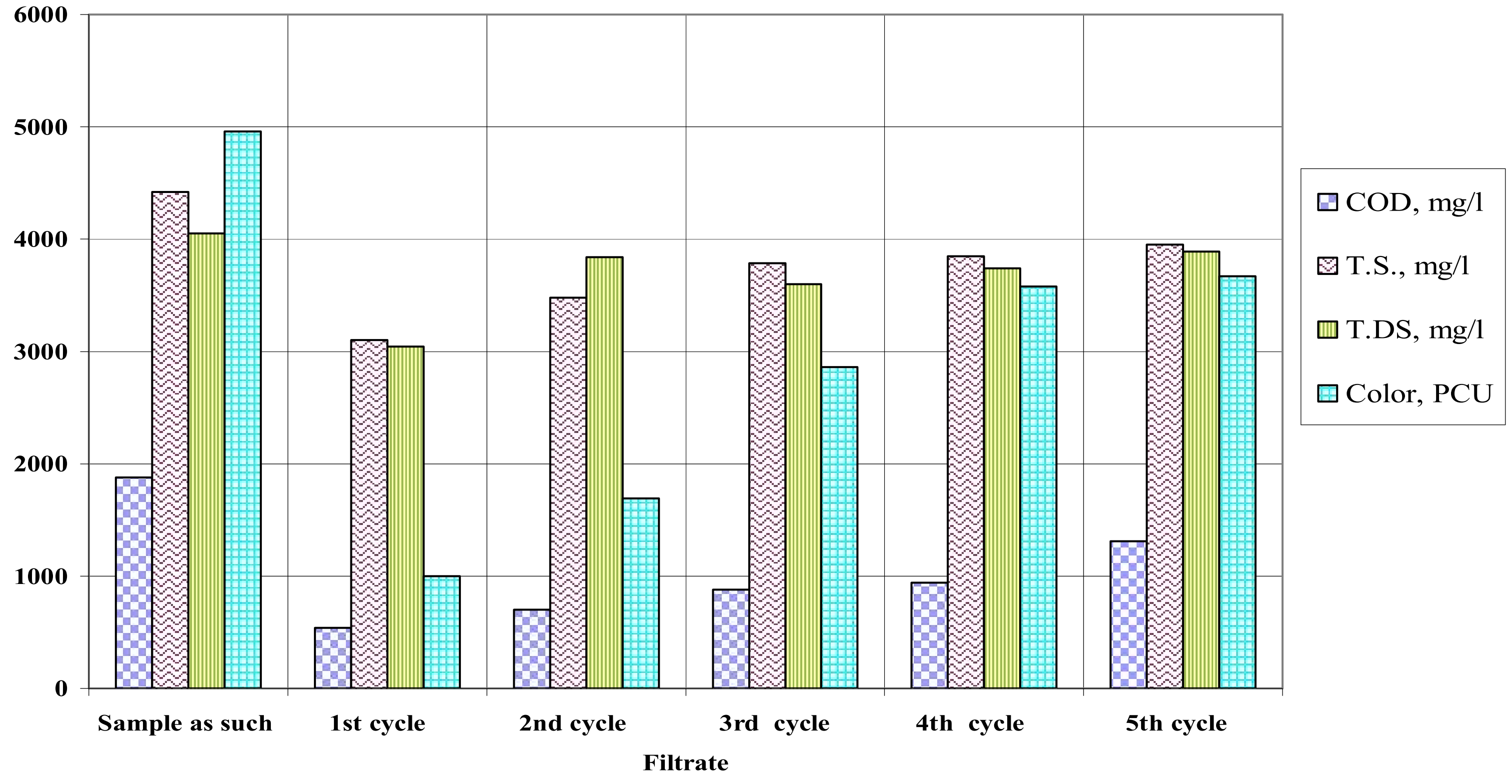

Fig 5.14 - Reduction in Pollution Load of Combined Bleach Effluent by use of Activated Carbon (Agro Based Mill)

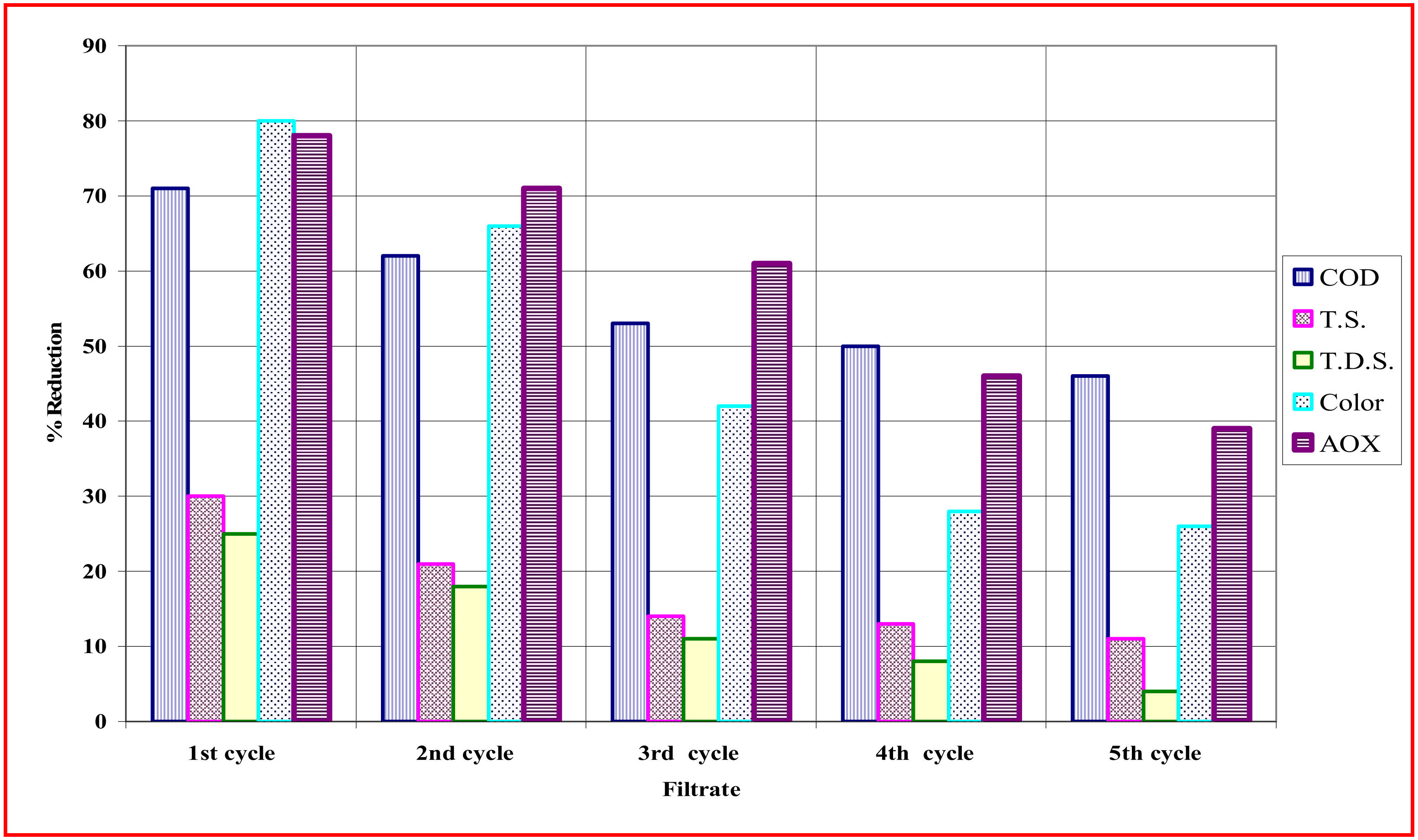

Fig 5.15 - % Reduction in Pollution Load of Combined Bleach Effluent by use of Activated Carbon (Agro Based Mill)

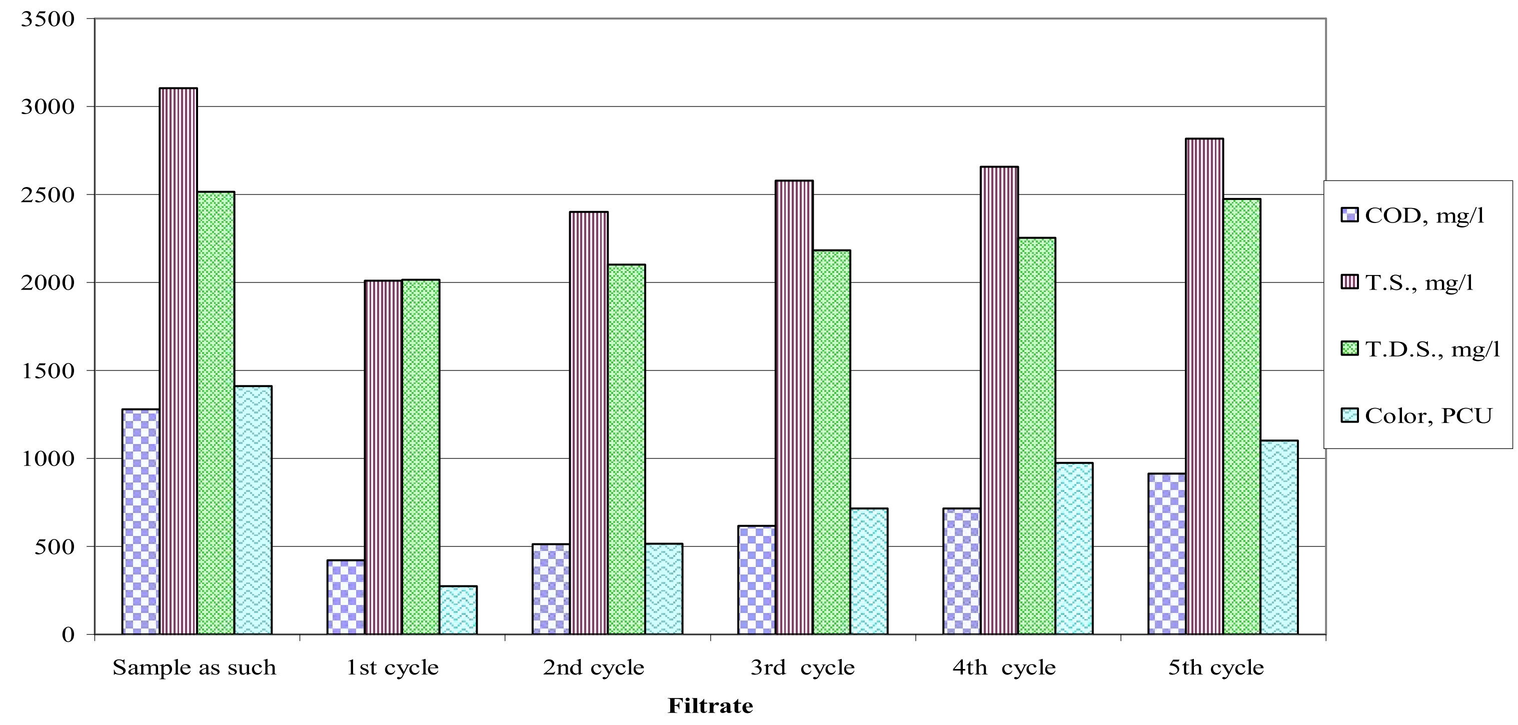

Fig – 5.16 Reduction in Pollution Load of Combined Bleach Effluent by use of Activated Carbon (Wood Based Mill), Sample-1

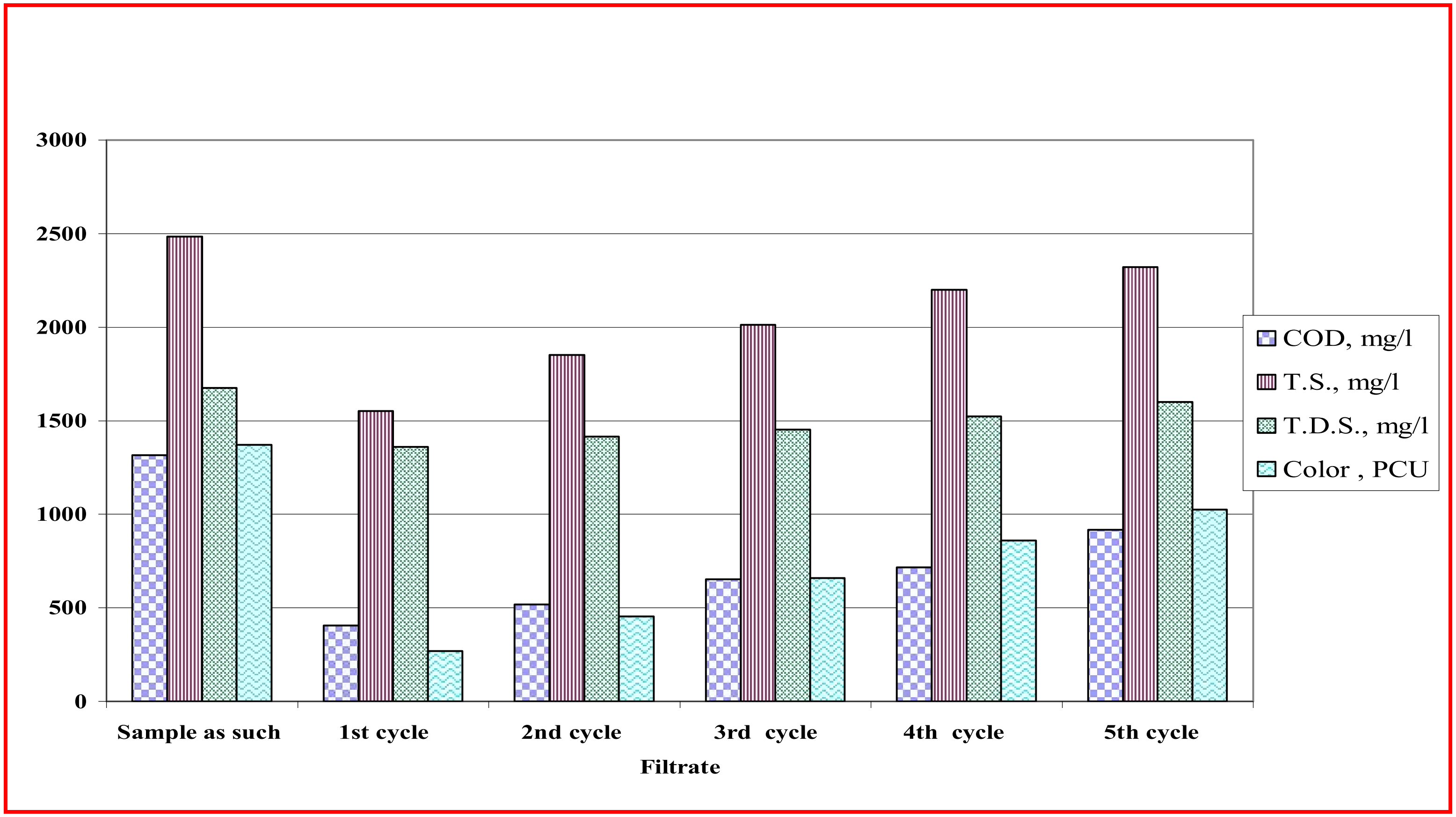

Fig 5.17 - Reduction in Pollution Load of Combined Bleach Effluent by use of Activated Carbon (Wood Based Mill), Sample-2

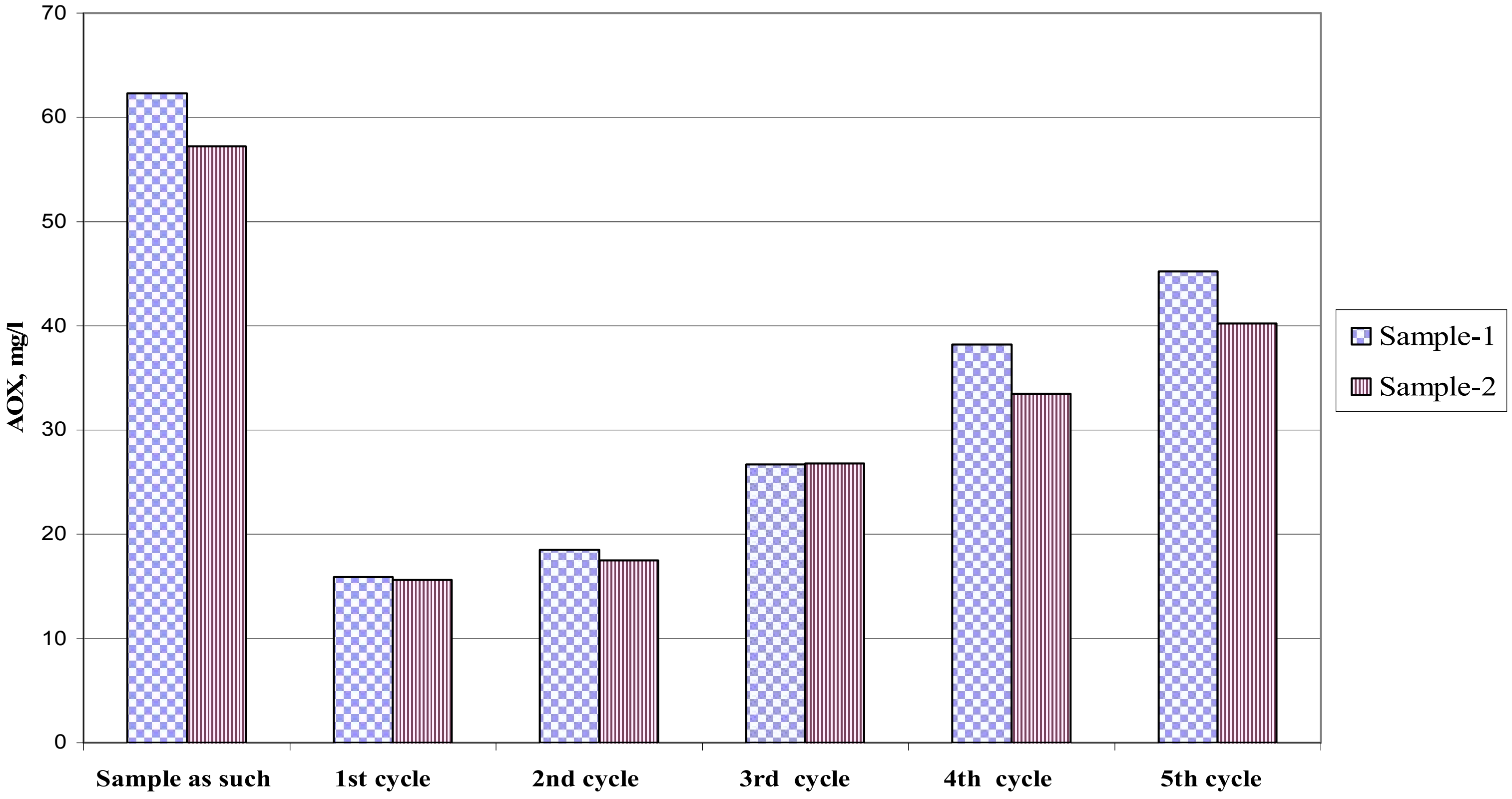

Fig 5.18 - Reduction in AOX of Combined Bleach Effluent by use of Activated Carbon (Wood Based Mill)

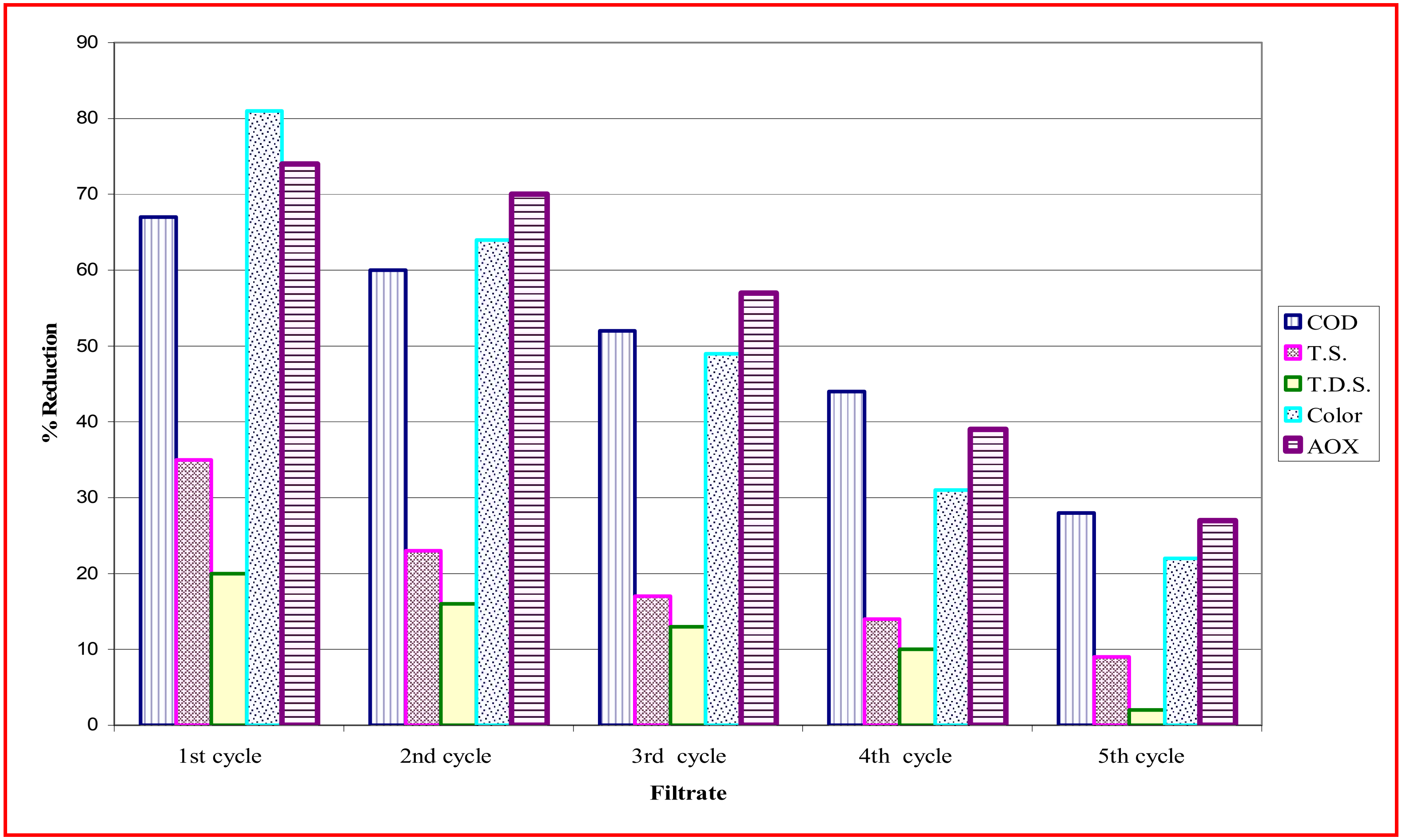

Fig 5.19 -% Reduction in Pollution Load of Combined Bleach Effluent by use of Activated Carbon (Wood Based Mill), Sample-1

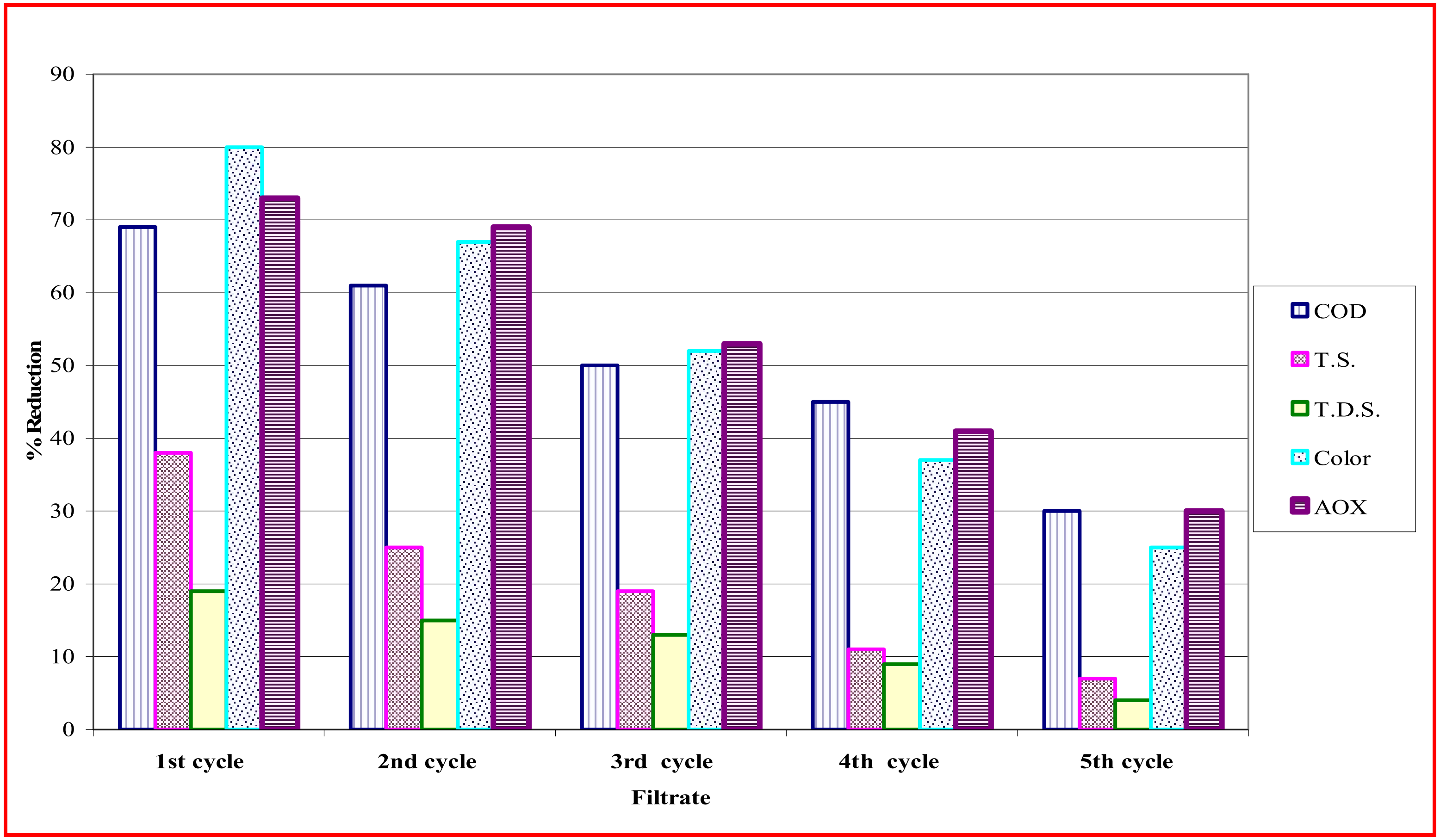

Fig 5.20 - % Reduction in Pollution Load of Combined Bleach Effluent by use of Activated Carbon (Wood Based Mill), Sample-2

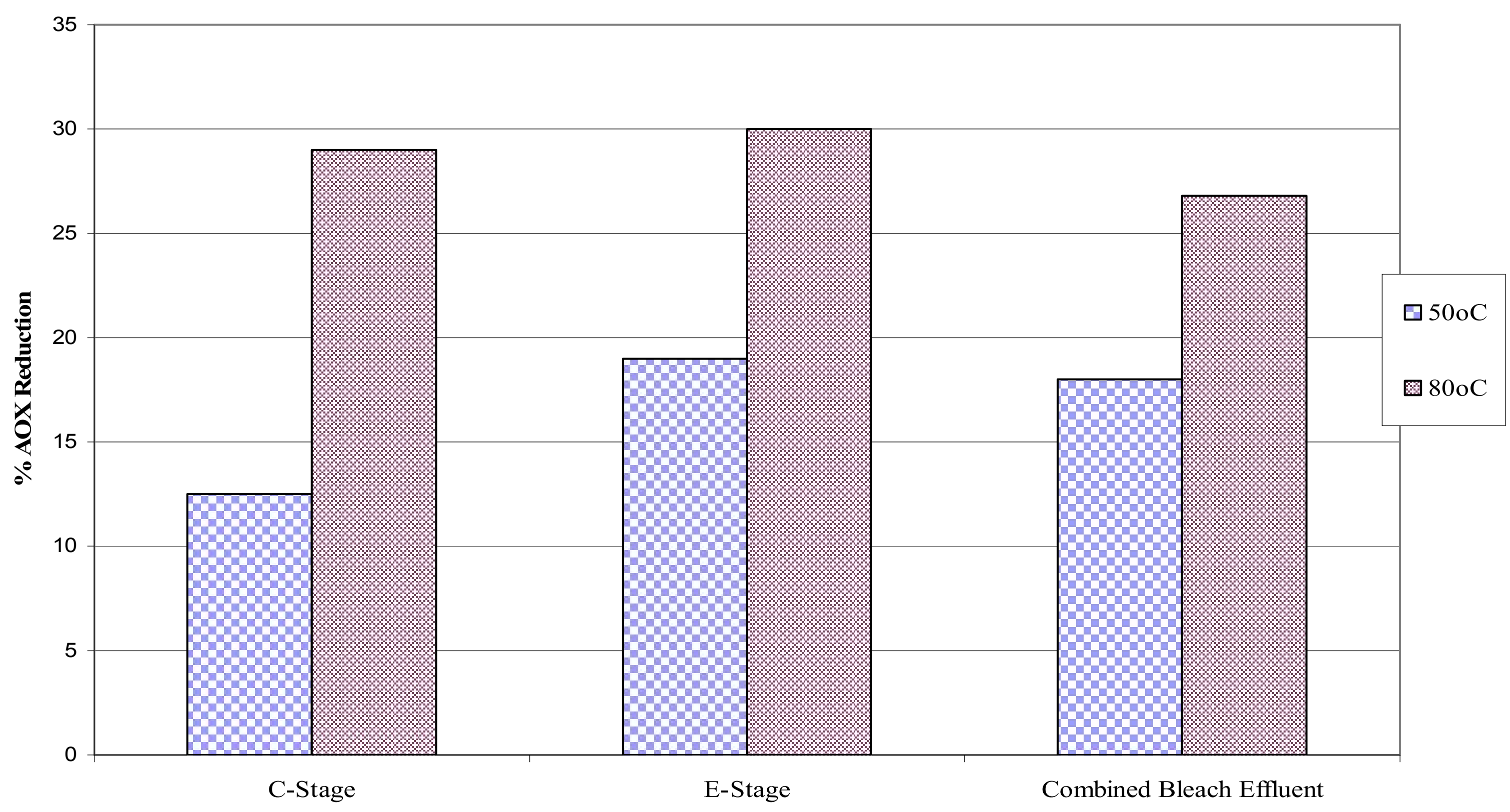

Fig 5.21 - % AOX Reduction by Thermal Treatment of Bleach Plant Effluent (Agro Based Mill)

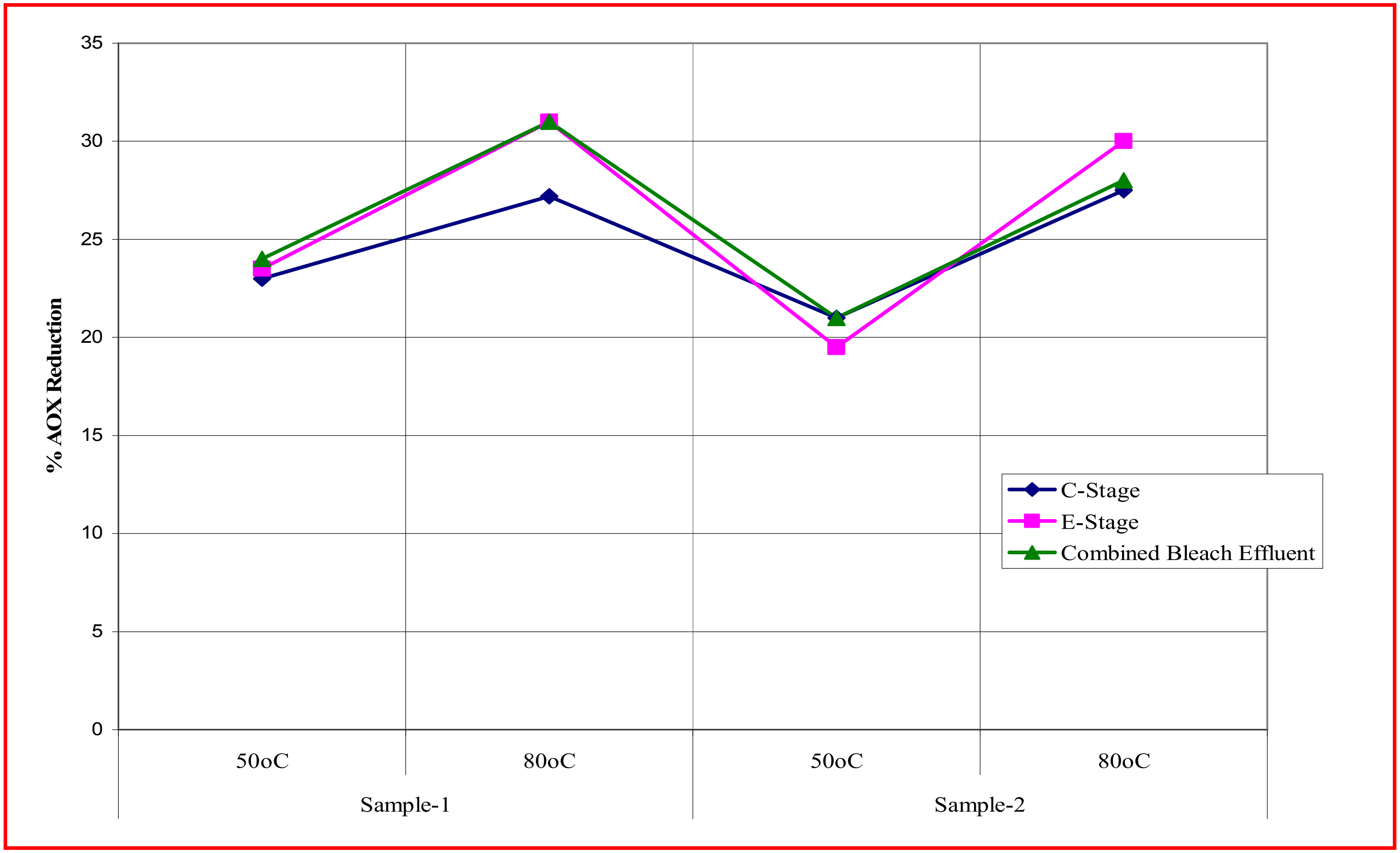

Fig 5.22 -% AOX Reduction by Thermal Treatment of Bleach Plant Effluent (Wood Based Mill)

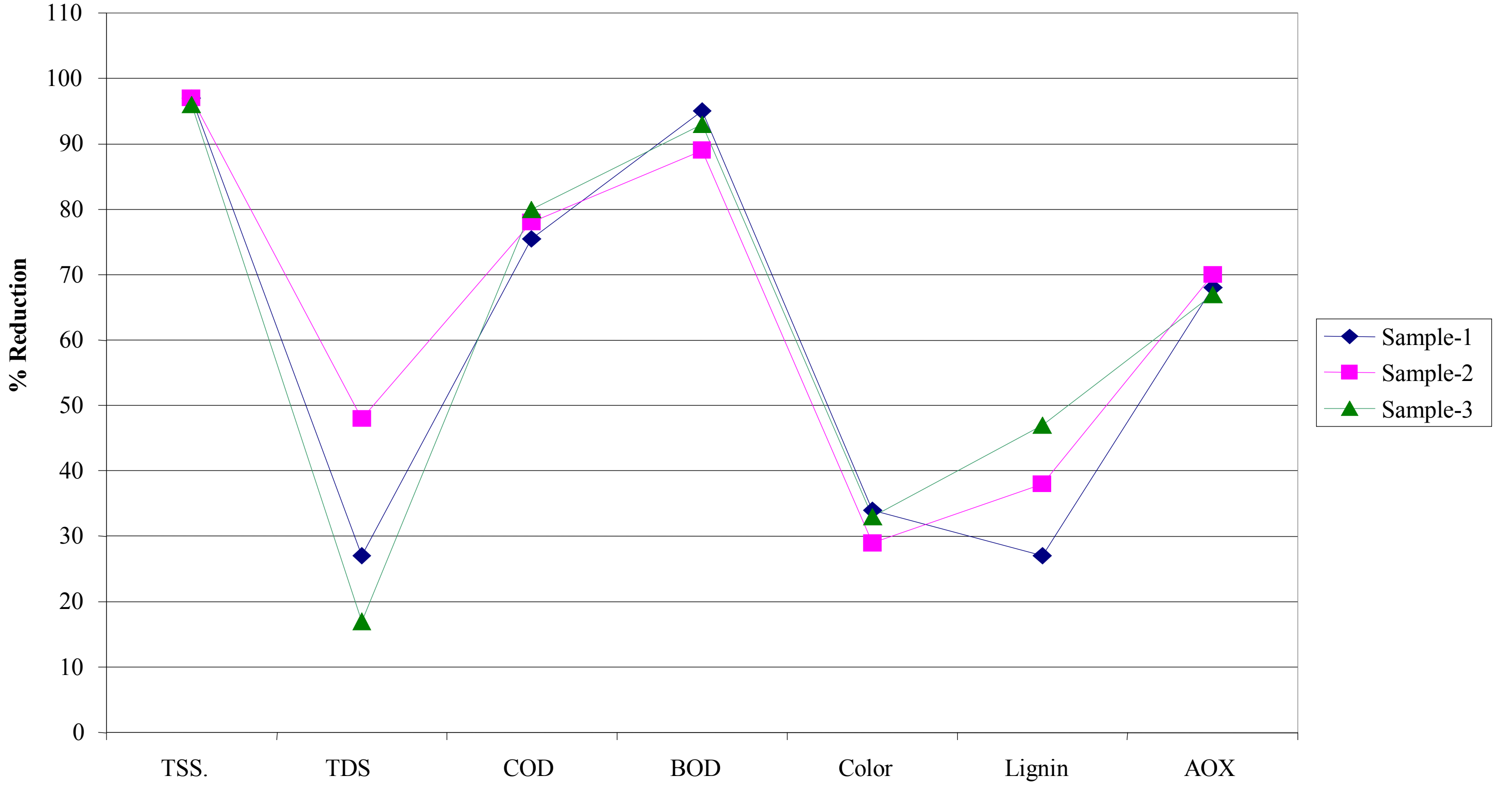

Fig 5.23 - Pollution Load Reduction in ETP Using Lime and Alum (Wood Based Mill)

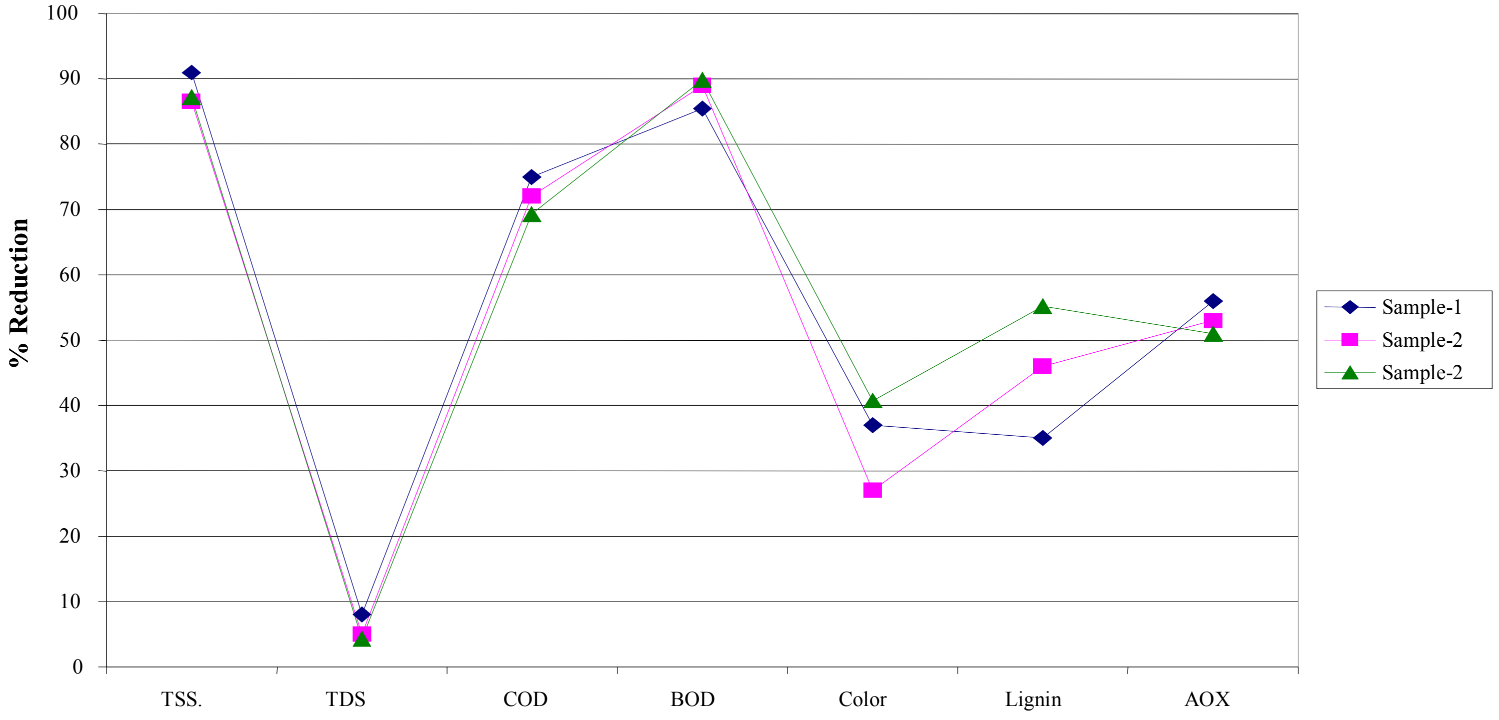

Fig 5.24 - Pollution Load Reduction in ETP without Lime and Alum (Wood Based Mill)

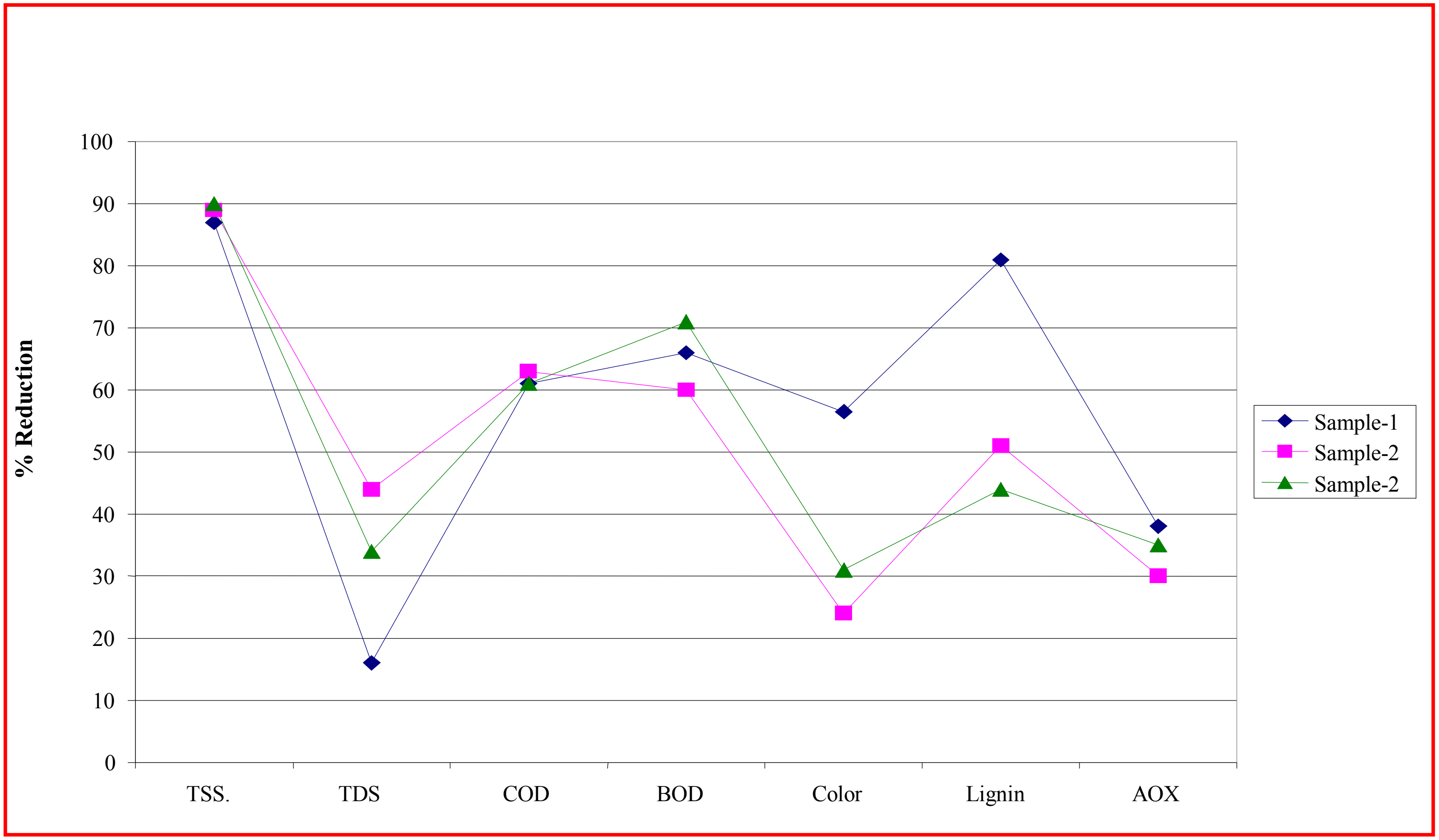

Fig 5.25 - Pollution Load Reduction in ETP without Lime and Alum (Agro Based Mill)

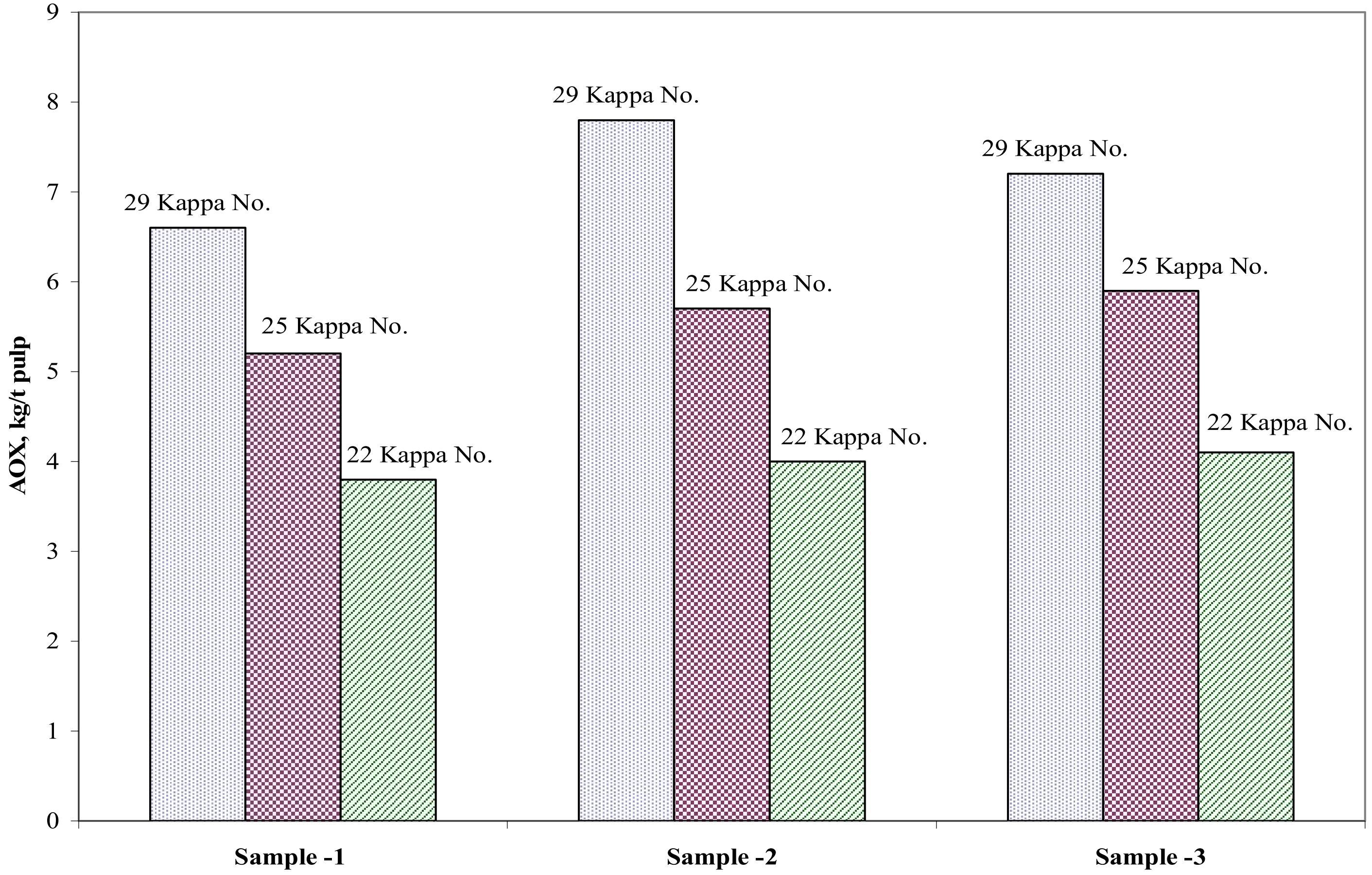

Fig 5.26 Effect of Kappa No. on AOX Level of Bleach Plant Effluent in Agro Pulp

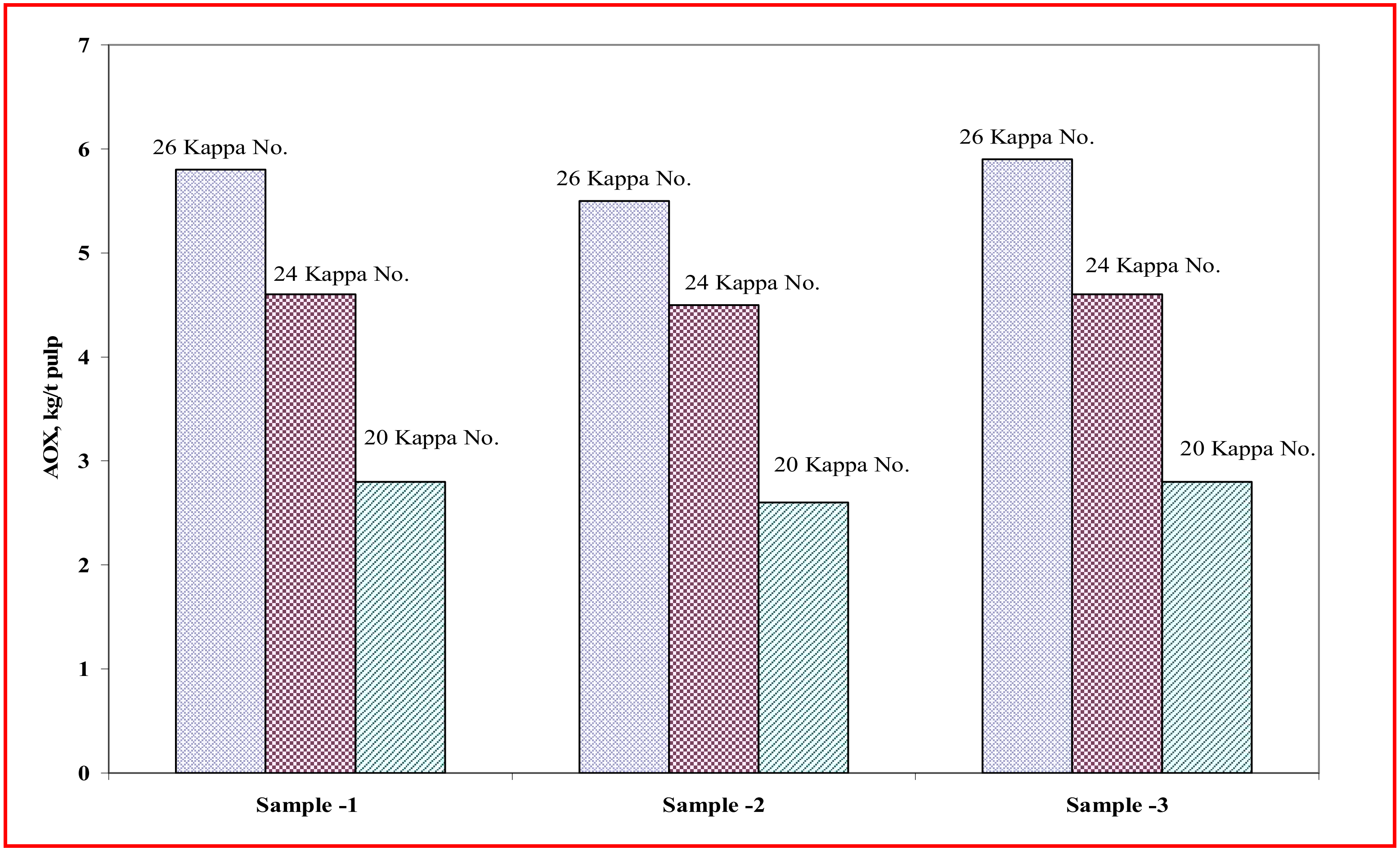

Fig 5.27 Effect of Kappa No. on AOX Level of Bleach Plant Effluent in Wood Pulp

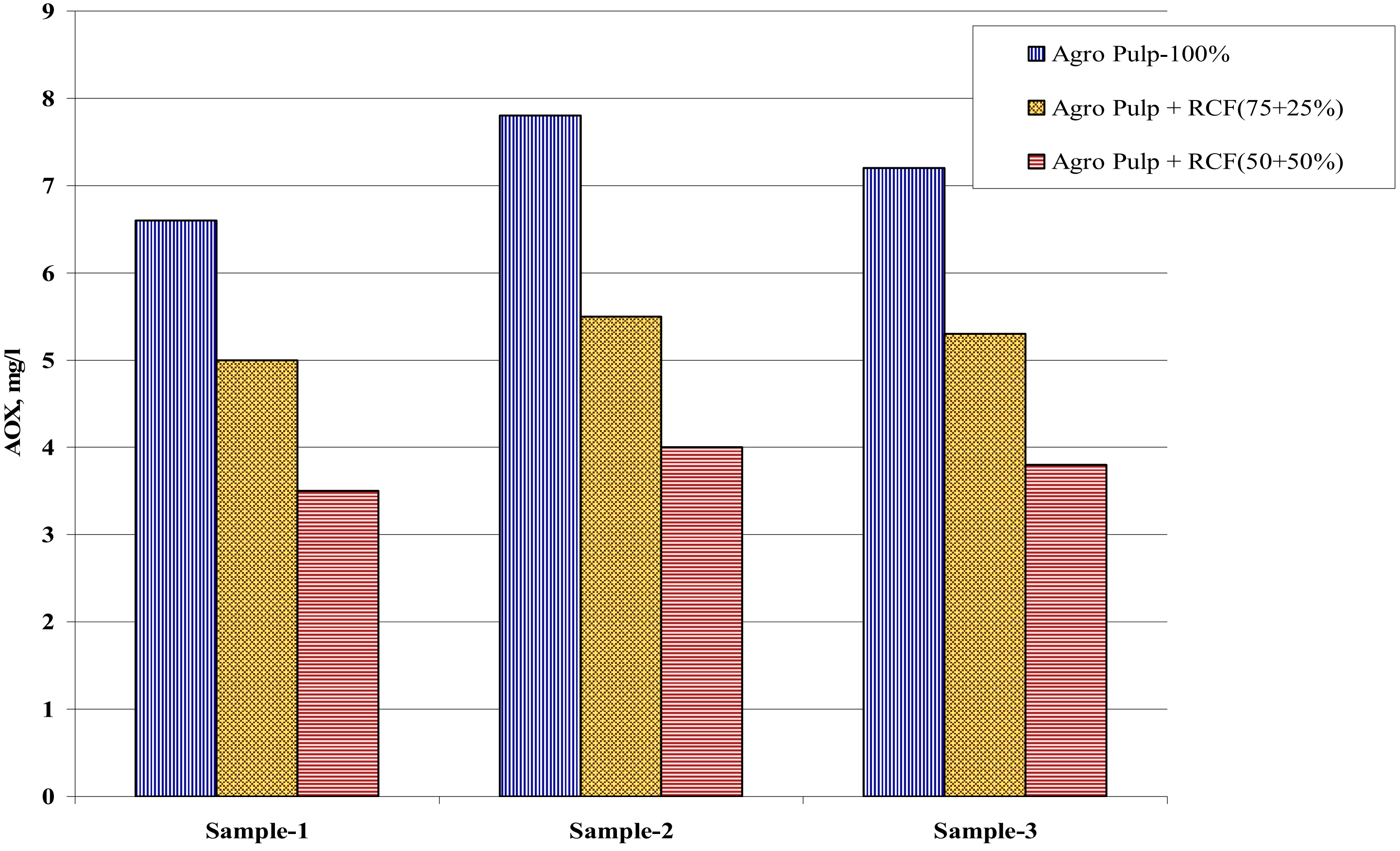

Fig 5.28 Reduction of AOX by Use of RCF with Agro pulp

CHAPTER-6.0

RESULTS & DISCUSSIONS

The present study has resulted in characterization of bleach plant effluent, evaluation of AOX level in Indian pulp and paper mills, evaluation of toxicity potential of AOX, evaluation of efficiency of at source and EOP treatment options in reducing AOX level.

6.1 CHARACTERISATION OF BLEACH PLANT EFFLUENT

The results of the studies carried out on characterization of bleach plant effluents collected from agro based mill and wood based mill for different pollutional parameter including AOX are indicated in the **Table 3.3, 3.4, 3.5, 3.6, 3.7 & 3.8.**

As indicated in the **Tables 6.1** and summarised under the bleach plant effluent of agro based mills have high AOX level compared to wood based mills.

- The level of AOX in the C-stage effluents in agro based mill was varying from 72 to 83 mg/l compared to wood based mill (41 to 55 mg/l).

- In the E-stage effluents of agro based mill the AOX level was 95 – 109 mg/l compared to wood based mill (88 - 98 mg/l).

- AOX level in H- stage of agro based mill was 45 – 65 mg/l & 46 -60 mg/l in wood based mill.

- AOX level in Combined bleach plant effluent of agro based mill was 55 – 76 mg/l compared to wood based mill (50 – 58 mg/l).

TABLE 6.1

AOX LEVEL IN BLEACH PLANT EFFLUENT IN INDIAN PULP AND PAPER MILLS

Bleach Plant Effluent	**Agro**	**Wood**
	AOX, mg/l	
C-stage	72 to 83	41 to 55 l
E-Stage	95 – 109	88 - 98
H-Stage	45 – 65	46 -60
Combined bleach plant effluent	55 – 76	50 – 58

- This due to the fact that in agro based mills major part of lignin is removed during bleaching stage instead of pulping due to economical reasons. Alkali being costly the mills produce high kappa pulp and consequently high quantity of chlorine or chlorine based chemicals are used in pulp bleaching to achieve desired brightness target level resulting in high level of AOX as compared to wood based mill.

- Other pollutional parameters like COD, BOD, Color, etc were also found to be higher in bleach plant effluent of agro mills in comparision to the wood based mill. The reason being in agro based mills the pulp washing is not very effective due to inherent fibre nature as well as poor performance of pulp washer leading to high carry over in the pulp and consequently use of excess bleaching chemical leading to high AOX load.

6.2 TOXICITY EVALUATION

The toxicity evaluation through fish mortality test and Microtox Toxicity (% inhibition) test carried out of bleach plant effluent collected from agro based mill and wood based mill.

6.2.1 FISH TOXICITY TEST (LC_{50})

Toxicity inhibition response of bleach plant effluents on fish mortality was evaluated for wood based and agro based mill & results are shown in **Table 4.1 to 4.10.** From results summarised in **Table- 6.2** , it has been observed that :

- C-stage effluent collected from wood based mill was found to be toxic to the fish between 40-50% & 35-37 % volume of effluent concentration in agro based mill.

- E-stage effluent collected from wood based mill was found to be toxic to the fish between 30-40% & 30-34 % volume effluent concentration in agro based mill. The result shows that E-stage effluent was more toxic than other stage effluent.

- H-stage effluent collected from wood based mill was found to be toxic to the fish between 57-65% & 43-47 % volume effluent concentration in agro based mill.

- Combined Bleach Plant effluent collected from wood based mill was found to be toxic to the fish between 50-50% & 40-44 % volume effluent concentration in agro based mill.

TABLE 6.2
FISH TOXICITY (LC_{50}) OF BLEACH PLANT EFFLUENT IN INDIAN PULP AND PAPER MILLS

Bleach Plant Effluent	Agro	Wood
	FISH TOXICITY LC_{50}	
	Volume Concentration of Effluent, %	
C-stage	35-37	40-50
E-Stage	30-34	30-40
H-Stage	43-47	57-65
Combined bleach plant effluent	40-44	50-50%

LC_{50} of E-stage bleach plant effluent was very less (in between 30-40 Volume Concentration of Effluent, %) of wood and agro based mills & this indicate that E-stage bleach plant effluent is highly toxic than the other bleaching stage effluent. Thus it is advised the mills may segregate the E stage bleach plant effluent and treat it separately before being discharged to the aquatic environment.

6.2.2 MICROTOX TOXICITY TEST (% INHIBITION)

Toxicity inhibition response of bleach plant effluents on Luminescent bacteria was evaluated using Microtox Toxicity Analyzer. The results obtained are shown in **Table- 4.11 -4.12** for wood and agro based mill respectively. The results are summarised in **Table 6.3** and it has been observed that-

- Inhibition of luminescent bacteria in C- stage effluent of wood based mill was observed between 65- 70 % and 70-80 % in agro based mill.

- Inhibition of luminescent bacteria in E- stage effluent of wood based mill was observed between 85-90 %and 85-95 % in agro based mill.

- Inhibition of luminescent bacteria in H- stage effluent of wood based mill was observed between 50-55 % and 52-65 % in agro based mill.

- Inhibition of luminescent bacteria in combined bleach effluent of wood based mill was observed between 65-70 % and 68-75 % in agro based mill.

TABLE 6.3

MICROTOX TOXICITY TEST (% INHIBITION) OF BLEACH PLANT EFFLUENT IN INDIAN PULP AND PAPER MILLS

Bleach Plant Effluent	**Agro Mills**	**Wood Mills**
	(% INHIBITION)	
C-stage	70-80	65- 70
E-Stage	85-95	85-90
H-Stage	52-65	50-55
Combined bleach plant effluent	68-75	65-70

- Maximum inhibition (>85%) was observed in E-stage bleach plant effluent of wood and agro based mills. This indicates that E-stage bleach plant effluent is highly toxic and needs to be treated before being discharged to the aquatic environment.

The microtox toxicity results reconfirm the toxicity potential of different bleach plant effluent streams

6.3 REDUCTION OF AOX LEVEL THROUGH PHYSICO – CHEMICAL TREATMENT

AOX reduction through different physico –chemical treatment studies has been evaluated under the study and the results are indicated below:

6.3.1 CHEMICAL TREATMENT

The response of simultaneous coagulation / precipitation by using alum, lime and PAA has been evaluated for treatment of bleach plant effluent collected from agro and wood based mills. Results obtained are indicated in **Table 5.1, 5.2 & 5.3** for agro based mill and **Table 5.4, 5.5 & 5.6** for wood based mill. The AOX reduction by chemical treatment of bleach plant effluents are summarised in **Table- 6.4** and it has been observed that -

- The results indicate that combination of chemicals (Lime, Alum and polymer) was quite effective in reduction of AOX and other pollution load in bleach plant effluents and around 51-56%, 52-61%, & 55-58% AOX reduction was achieved in C- stage , E- stage & combined bleach plant effluent of agro based mill respectively .

- Around 68-71%, 61-77% & 61-71% reduction in COD was achieved in C-stage, E-stage and combined bleach effluent respectively collected from agro based mill. Reduction in colour level was between 78-86%, 86-89% & 71-82% in C-stage, E-stage and combined bleach effluent respectively of agro based mill

- AOX reduction in bleach plant effluent of wood based mill achieved between 50-63%, 56-69% & 54-65 % in C-stage, E-stage and combined bleach effluent respectively.

- Similarly COD reduction was between 72-79%, 71-84% & 68-76% and color reduction between 82-84%, 73-89% & 88-94% in C-stage, E-stage and combined bleach effluent respectively collected from wood based mill.

TABLE 6.4

AOX REDUCTION BY CHEMICAL TREATMENT OF BLEACH PLANT EFFLUENT IN INDIAN PULP AND PAPER MILLS

Bleach Plant Effluent	**Agro Mills**	**Wood Mills**
	(% AOX Reduction)	
C-stage	51-56	50-63
E-Stage	52-61	56-69
Combined bleach plant effluent	55-58	54-65

- It has been observed that the chemical treatment also results in reduction of toxicity of bleach plant effluent. About 53-57% and 47-53% reduction in toxicity of E-stage and combined effluent respectively of agro based mill and 56-59% and 57-62% reduction in E-stage and combined effluent respectively of wood based mill could be achieved after chemical treatment.

6.3.2 CARBON ADSORPTION

- Carbon adsorption technique has also been evaluated for treatment of bleach plant effluent (E-stage) collected from a wood-based mill. Effluent passed through a column filled with activated carbon and the results obtained is depicted in **Table- 5.9, 5.10 & 5.11 Fig- 5.13 to 5.20.**
- Though initially the carbon filter was highly efficient in reduction of pollution load as reduction in AOX. However subsequently the

reduction efficiency of carbon filter decreased and the carbon bed needs to be recharged.

- The reduction of AOX declined from 78% to 24% and 74 % to 27% after 5th filtration cycle of bleach plant effluent of agro and wood based mill respectively. The reduction of COD decreased from 71% to 30% and 69% to 28% after 5th filtration cycle of agro and wood based mill respectively.

- The color reduction efficiency decreased from 80 to 26% and 81 to 22% after 5th filtration cycle of bleach plant effluent of agro and wood based mill through activated carbon respectively.

- Carbon filter though effective but has limitations in context of handling huge volume of effluent load as well as need to recharge the filter bed after regular intervals.

- It may be used in combination with prefilter / pre-treatment in order to have an enhanced efficiency of carbon.

6.3.3 THERMAL TREATMENT

- The impact of thermal treatment of bleach plant effluents was carried out to study the AOX reduction potential. The results obtained are shown in **Table 5.12 to 5.14 and Figs. 5.21 & 5.22.**

- It has been observed that the reduction in AOX is not significant as compared to chemical treatment, electrofloculation or carbon filter techniques.

- The reduction of AOX in C-stage effluent at 50°C and 80°C was around 12.5-23% and 27-29% respectively.

- The reduction of AOX in E-stage effluent at 50°C and 80°C was around 19-23.5% and 30-31% respectively and in combined effluent the reduction at 50°C and 80°C was around 18-24% & 27-31% respectively.

6.3.4 BIOLOGICAL TREATMENT

AOX reduction through biological treatment (activated sludge process) of combined mill effluent was also studied in different mills. The results are given in the **Table 5.15 to 5.23 and Fig 5.23 to 5.25.**

- The reduction in AOX was about 67-70% after using lime and alum prior to biological treatment while the 51-56% reduction in AOX was achieved without using lime & alum.

- The reduction in AOX was less (30-38%) in small scale agro based mills as compared to wood based mill (51-56%).

- The reason for low reduction of AOX in agro based was
  - ✓ High level of AOX
  - ✓ Inadequate ETP
  - ✓ Low MLSS level
  - ✓ Low D.O. level

- To achieve a higher level of pollution load reduction including AOX adherence to optimal ETP operating parameters is of utmost importance

6.3.5 IN HOUSE OPTIONS TO CONTROL AOX DISCHARGE LEVEL

As there are limitations before the Indian pulp & paper mills in adopting modern fiber line technologies (as discussed in Chapter 2) for reducing AOX level due to reasons mentioned earlier , other options as mentioned under involving better house keeping , process optimisation etc apart from End of Pipe Treatment Methods discussed above can be adopted to reduce the AOX level .

6.3.5.1 CONTROLLED PULP MILL OPERATION

As indicated in **Table –5.24 & 5.25 & Fig-5.26 – 5.27** reducing the Kappa no. from 26 to 20 the AOX level reduced by 51.7 to 52.7 % in wood pulp and however reducing the Kappa No. from 29 to 22 the AOX level reduced by 42.2 - 44.4 % in agro pulp using same bleaching sequence.

The mills must carry out pulping to achieve Kappa No. below 20. Reducing the Kappa No. will help in reducing the bleaching chemical consumption and accordingly reducing AOX level.

6.3.5.2 ADOPTION OF IMPROVED PULP WASHERS

New generation pulp washers like belt washers, twin drum washers etc will help in efficient extraction of black liquor from the pulp and consequently reduce the COD carryover and bleaching chemical requirement leading to reduced AOX level.

6.3.5.3 INCREASED USE OF RECYCLED FIBER

The mills can substitute apart of agro chemical pulp with recycled fiber pulp so as to reduce the over all bleach demand and accordingly AOX level.

CHAPTER – 7.0

CONCLUSION & RECOMMENDATIONS

Based on the study carried out and interaction with the mills the major conclusions are summarized as under:

- The bleach plant effluent is one of the main environmental concerns in the pulp and paper mills in context of AOX level.

- The discharge of AOX in Indian pulp and paper mills is comparatively high as most of these mills use high dosages of chlorine to bleach the pulp to achieve high brightness.

- The main issues before the Indian paper industry in context of discharge and control of AOX are –
  - Customer requirement of high brightness quality paper.
  - Cost competitiveness.
  - Environmental protection- high level of AOX.

- Though modern fiber line technologies like ODL , ECF bleaching etc are available for reducing AOX level, their adoption in Indian context specially in agro based is limited due to low scale of operation, use of mixed fibrous raw material depending upon seasonal availability and high capital investment / operational cost as well as lack of chemical recovery.

- As these mills are still carrying on with conventional pulping and chlorine based bleaching processes the strategy / approach to reduce AOX level will involve three way approach :

  - In house Control Measures.
  - End of pipe(EoP) treatment.
  - Integrated Approach (combination of In-house & EoP Treatment)

➢ The major in house measures for AOX reduction include:

- Optimization of process operations
- Producing low kappa pulp below 20
- Improved efficiency of pulp washers to ensure low COD carry over
- Use of oxidative alkali extraction
- Optimization of fiber furnish , increased used of RCF in fiber furnish ,
- Control of spillages of bleach plant effluent through setting up of collection tanks & seal pits, etc
- Segregation of highly polluted streams and less polluted streams for appropriate treatment
- Small agro based mills should expand their pulp mill capacity to install chemical recovery system or if it is not possible, they should restrict pulp production and should use recycled fiber in fiber furnish.
- If the bleaching chemicals are not rapidly & uniformly distributed through the pulp, there is chance of a portion of pulp being over bleached as such optimum bleach chemical requirement should be determined and accordingly appropriate measures should be adopted to improve the mixing of bleaching chemicals along with the pulp so as to have minimum residual chlorine in bleach plant effluent and reduce the level of AOX

- The high level of AOX, COD, colour and inorganic salts restricts reuse of bleach plant effluent into the internal process.

- The results of chemical treatment of bleach plant effluent using lime and alum (usually used by the pulp and paper mills) have been found to be effective in reduction of AOX about 51-61 % along with COD 61-77%, Color 71-89% etc .

- The use of chemicals for treatment of bleach plant effluent has an additional advantage of reduction of COD & color in addition to AOX removal which ultimately reduce operating cost of subsequent ETP.

- Activated carbon is also very effective in reduction of AOX in bleach plant effluent but it has the limitation of need of frequent recharging of carbon filter.

- Chemical treatment of bleach plant effluents with lime and alum of bleach plant effluent reduce the toxicity and no fish toxicity was observed on exposing for 96 hrs with chemically treated bleach plant effluent.

- AOX reduction can be achieved very efficiently through biological treatment process after chemical treatment of influent.

- An integrated approach involving better house keeping, optimisation of process variables, restricting the chemical pulp production , increasing the recycled fiber proportion in the fiber furnish , optimal use of effluent treatment plants etc., as well as application of appropriate physic- chemical treatment can help in reducing AOX as well as its overall environmental impact is required to be adopted to reduce AOX.

CHAPTER - 8

REFERENCE

1) Axegard P., (1989), "Improvement of bleach plant effluent by cutting back on Cl_2", Pulp & Paper Canada, 90:5

2) Amendola, G. (1989), "The occurrence and fate of PCDDd and PCDFd in 5 bleached Kraft pulp and paper mills", Chemosphere 18, No. 1-6. pp. 1181-1188

3) Ali, M & Sreekrishnan, T.R. (2001), "Aquatic toxicity from pulp & paper mill effluents: a review", Adv. Environmental Research ,5, 175-196

4) Ahtiainen, J., Nakari T., & Silvonen, J. (1996) "Toxicity of TCF & ECF pulp bleaching effluents assessed by biological toxicity tests" Book on Environmental Fate & Effects of Pulp & Paper Mill Effluents, Edited by Mark R. Servos, Kelly R. Munkittrick, John H. Carey, Glen J. Van Der Kraak, 3-20

5) Bergman, A., Pilotti, A. & Renberg, L. (1994), "Potential Formation of Chlorinated By-products in Industrial Processes", Publ. Swedish National Chemicals Inspectorate 13pp & Appendices

6) Boddington, M.J., Douglas, C.E., Duncan, M., Gilbertson, D.L., Hallett, D., McDlelland, L., Roberts, J.R., Sing, J.,& Whittle, M. (1983), "Dioxins in Canada", Chemosphere 12, No 4/5. pp. 477-480.

7) Bruce I. Fleming , (1995),"Organo chlorine in perspective", TAPPI International Environmental Conference proceedings

8) Banerjee S., Kemeny T.E., R.Sackellare & M.D.Juszynsk, (1996), "AOX & COD removal in the activated sludge basin" TAPPI International Environmental Conference, 159-162

9) Bajpai P. and Bajpai P.K, (1994), "Biological colour removal of pulp and paper mill wastewater", J Biotechnol. 33:211-220

10) Bloomberg, L., Talka, E., Valtilla, O, (1990) , Organic carry over in kraft pulp and bleaching discharge, pulping conference, Tappi, 217-226

11) Bergbauer, M. and Eggert, C., (1992), "Differences in the persistence of various bleachery effluent lignins against attack by white-rot fungi", Biotechnology Letters Volume 14 No.9 (Sept.) pp.869-874

12) Boddington, M.J. (1984), "the dioxin issue - an overview", Chemosphere 14, No. 6/7. pp. 721-727.

13) Cook, D.L., Parish, A., Borton, D.L. & Hall, T., (1998) "A summery of pulp and paper mill experience with toxicity reduction and toxicity identification evaluations", Proceedings of Environmental Conference, TAPPI, Book-3

14) CPPRI annual Reports and Project reports

15) Clement, R.E., Tashiro, C., Suter, D., Reiner, E., & Hollinger, D. (1989), "Chlorinated dibenzo-p-dioxins (cdds) and dibenzofurans (cdfs) in effluents and sludges from pulp and paper mills", Chemosphere 18, No 1-6. pp. 1189-1197.

16) Chaparro, T.R., Botta, C.M. & Pires, E.C., (2010) " Toxicity and recalcitrant compound removal from bleaching pulp plant effluents by an integrated system: anaerobic packed bed bioreactor and ozone" Water Science & Technology- WST, 61.1 199-205

17) Cook, C.R. (1990), "Organochlorine discharges from a bleached kraft pulp mill with oxygen delignification and secondary treatment system", pulp & Paper Canada 91 (8): T 305

18) Cox, E.A., and Finnecy, E.E. (1986), "Dioxins and waste disposal: the UK experience", Chemosphere 15, No 9/12. pp. 1543-1548.

19) Carlberg, G.E, Kringstad A, Martinsen K & Nashaug O, (1987), “Environmental Impact of Organochlorine Compounds Discharged from the Pulp and Paper Industry”, Paperi Puu, 69(4), 337-341

20) Johannes, D.L. and Lowe, R.W. (1992), “AOX testing of bleach plant effluents – a discussion of laboratory methods”, Pulp & Paper Canada, 93:9 37

21) Easton et al. (1997), “Genetic Toxicity of Pulp Mill Effluent on Juvenile Chinook Salmon (Onchorhynchus shawytscha) Using Flow Cytometry”, Elsevier Science Ltd., Vol. 35, #2-3.

22) Earl P.F., & Reev D.W., (1989), “Chlorinated organic matter in bleached chemical pulp production part : III – The effects of chlorination stage variables on formation of chlorination stage compounds”, TAPPI 72(10):183

23) Eklund, B., Linde M. & Tarkepea, M. (1996) **“**Comperative assessment of the toxic effects from pulp mill effluents to marine brackish water organisms”, Book on Environmental Fate & Effects of Pulp & Paper Mill Effluents, Edited by Mark R. Servos, Kelly R. Munkittrick, John H. Carey, Glen J. Van Der Kraak, 3-20

24) Edde, H. (1994) “Techniques for closing the water circuits in the pulp and paper industry”, Water Science and Technology 29 (5-6): 11-18

25) Fortunati, G.U. (1984), “The Seveso Accident”, Chemosphere 14, No. 6/7. pp. 729-737.

26) Frostell, B., Boman, B., Mats Ek , B.Palvall, M.Berglund & A. Lindstrom, (1994), “Influence of bleaching condition & membrane filtration on pilot scale biological treatment of kraft mill bleach plant effluent”, water Science & Technology, Vol.- 29 , No.-5-6, 163

27) Francis , D.W. , P.A. Turner, J.T. Wearing (1998), AOX reduction of kraft bleach plant effluent by chemical pretreatment—Pilot-scale trials , Pulp and Paper Research Institute of Canada, 24 July, www.sciencedirect.com/science/article/pii/S0043135497000584

28) Fraser J.L. & Reeve D.W., (1992), "Chlorinated organic matter in bleached chemical pulp production- an inter laboratory comparison of techniques and test results for AOX analysis in effluents", Pulp & Paper Canada 93:5 43

29) Gergov, M., Priha, M., Talka, E. & Valttila, O., (1988) "Chlorinated organic compounds in effluent treatment at kraft mills", TAPPI Journal December pp. 175–184 .

30) Gordon, R.C., Patricia L.Orr, Robertson, J.L. and Vrooman, W.M., (1990**),** "Toxicity and bioaccumulation of AOX & EOX", Pulp & Paper Canada, 91:9 , 39

31) Gonzales, P., Zaroor, C., (2000), "Effect of process modification on AOX emission from kraft pulp bleaching", Journal of Cleaner Production , 8 , 233-241

32) Hise, R.G. & Hintz, H.L. (1990). "The Effect of Brown Stock Washing on the Formation of Chlorinated Dioxins and Furans During Bleaching", TAPPI 73 (1), 185

33) Hickman, G. & Mathews L., (1995), **"**Bleached sulfite mill effluent & AOX treatment", TAPPI International Environmental Conference proceedings

34) Hocking, J. (1991), "Regulation of discharge of organochlorines from pulp mills in Canada", Environ. Manage. 15 (2): 195-204

35) Harrison, K. and Hoberg, G. (1994), "Risk, science, and politics – regulating toxic substances in Canada and the United States", McGill-Queen's University Press, Montreal, Quebec.

36) Hickman, G.T. &.Miller, J.P., (1993), "Toxicity reduction in bleached kraft mill effluent ", TAPPI, International Environmental Conference proceedings,261-279

37) International Standard (I.S.) 6582 1971

38) Juha, P.T.Fiskari, and Perttik K.Hynninen, (2000), "Toxicity in TCF bleach plant closures : laboratory experiments", International Environmental Conference & Exhibit, TAPPI

39) Kringstadt, K.P. & Lindstrom K. (1984) “Spent liquors from pulp bleaching”, Environmental Science and Technology 18 (8): 236A-248A

40) Kociba, R.J. and Keyes, D.G. (1978), “Results of a two-year chronic toxicity and oncogenicity study of 2,3,7,8-TCDD in rats”, Toxicology and Applied Pharmacology 46: 279-303

41) Kerski, A. (1995) Pulp, “Paper and Power: How an industry reshapes its social environment”, Ecologist 25 (4): 142-148

42) Lindsay, K. and Smith, D.W. (1995), “Factors influencing kraft pulp mill effluent treatment in Alberta”, Journal of Environmental Management, 44: 11-27.

43) Larsson, L., T. Andersson, L. Forlin and J. Hardig, (1988). "Physiological Disturbances in Fish Exposed to Bleached Kraft Mill Effluents", Water Sci. Technol., 20(2): 67-76

44) LaFleur, L., Bousquet, T., Ramage, K., Brunck, B., Davis, T., Lukesemburg, W., and Peterson, B. (1990),” Analysis of PCDD and PCDF on the ppq-levels in milk and food sources”, Chemosphere 20, No. 10-12. pp. 1657-1662.

45) McDonough, T. (1992), Bleaching Agents (Pulp and Paper) In: Volume 4. Grayson, M. (Ed). Kirk-Othmer Encyclopedia of Chemical Technology. 4th Edition. pp301-311

46) Maybury, R., Singh, J., and Riedel, D. (1982), “2,4-D Herbicides: their chemistry, fate and effect on animals and humans”, Health and Welfare Canada (draft report), Ottawa

47) Myreen, B. (1994), “Pulp and paper manufacture in transition”, Water Science and Technology 29 (5-6): 1-9

48) Mohta, D., Upadhyaya, J.S., “Environmentally Friendly Pulping andBleaching of Bagasse”, http://www.tappi.org/Downloads/unsorted

49) Minor, J., Grayson, M. (Ed), (1982) Kirk-Othmer Encyclopedia of Chemical Technology. 3rd Edition. Publ. John Wiley & Sons, New York. pp379-419

50) Mall, I.D., Upadhyay, S.N. Singh, A.R., Upadhya, Y.D. (1989), "Environmental pollution due to pulp and industry" , IPPTA Seminar,

51) Milosevich, G.M. & Hill, D.A., (1992), "Reduction of AOX Bleach plant effluent by addition of Mill process alkalis", Pulp & Paper Canada, 93:3, 61-67

52) Martinsen, K., Kringstad,A., Carl Berg, G., (1988), "Methods for determination of sum parameters and characterization of organo chlorine compounds", Water science & Technology 20 (2):13 -24

53) Milstein, O., Haars, A., Majcherczyk, A., Trojanowski, J., Tautz, D., Zanker, H. and Huttermann, A. (1988), Removal of Chlorophenols and Chlorolignins from Bleaching Effluent by Combined Chemical and Biological Treatment, Water Science & Technology Vol 20 No 1 pp 161–170

54) Murray W. D.& Mark Richardson, (1993), "Development of biological and process technologies for the reduction and degradation of pulp mill wastes that pose a threat to human health", Critical Reviews in Environmental Science and Technology, Volume 23, Issue 2, 157-194

55) Neilson A.H., Allard A., Hynninger, M. Remberger, (1991), "The environmental fate of chlorophenolic constitute of bleaching effluents" TAPPI Journal 73 (8) 239-247,

56) Nelson A.H., Allard A.S., Hynning P.A., Remberger M., & Viktor T., (1990), "The environmental fate of chlorophenolic constitutes of bleachery effluents", TAPPI J. 73 (3) 239

57) Norstrom, R.J., and Simon, M. (1983), "Preliminary appraisal of tetra-to octachlorodibenzodioxin contamination in eggs of various species of wildlife in Canada", In, J. Miyamoto et al. (ed). IUPAC Pesticide Chemistry, Human Welfare and Environment, Pergamon Press, New York. pp. 165-170.

58) NRCC (National Research Council of Canada), (1981), "Polychlorinated dibenzo-p-dioxins: criteria for their effects on

man and his environment", Associate committee on Scientific Criteria for Environmental Quality, NRCC #18574. 251

59) Nielson, A.H., Allard, A.-S., Hynning, P.-A. & Remberger, M. (1991) "Distribution, fate and persistence of organochlorine compounds formed during production of bleached pulp", Toxicology and Environmental Chemistry . 30: 3-41

60) Owens, J.W., Swanson, S.M. & Birkholz, D.A. (1994) "Bioaccumulation of 2,3,7,8- tetrachlorodibenzo-p-dioxin 2,3,7,8-tetrachlorodibenzofuran and extractable organic chlorine at a bleached-kraft mill site in a Northern Canadian river system", Environmental Toxicology and Chemistry 13 (2): 343-354

61) O' Connor, B.E., Kovacs,T.C.,Voss, R.H., & Martel, P.H., (1993), "A study of the relationship between laboratory bioassay response and AOX content for pulp mill effluents" , Journal of Pulp and Paper Science 19 (1)

62) Olaf ,D, & Ingrid,H. (1993), "Chemical Composition of effluents from chlorine dioxide bleaching of kraft pulps before and after secondary effluent", International Environmental Symposium, Paris – 27-29 April

63) Odendahl, S.M., Weishar, K.M.& Reeve, D.W., (1990), "Chlorinated organic matter in bleached chemical pulp production: A review of measurement techniques for effluents", Pulp & Paper Canada, 91:4

64) Priha, M.H. & Talka, E.T., (1987) "Biological activity of bleached kraft mill effluent (BKME) fractions and process streams", Pulp & Paper Canada, (12): 143-144

65) Paul A. Johnston, R.L.Stinger, David Santillo, (1996), "Towards Zero Effluent pulp and paper production" Green Peace Research Laboratories, November

66) Panwar, S., Mishra, S., Endlay, N., Mathur, R.M. & Kulkarni, A.G. (2004), "Toxicity Reduction of Bleach Plant Effluent by using Chemical Additives", Ippta Vol.16. No2 July

67) Pokhrel, D. & Viraraghavan, T. , (2004),Treatment of pulp and paper mill wastewater—a review,Science of The Total Environment, Volume 333, Issues 1-3, 15 October, 37-58

68) Prasad, D.Y., Joyce, T.W., (1993**),** "Sequential treatment of E1 stage kraft bleach plant effluent", Bioresource Technology Volume 44, Issue 2, 141-147

69) Presley, J.R., (1996), **"**Bleach plant faces new environmental hurdle in Adsorbable Organic Halide (AOX)", Book on Environmental Solution – Advances in Effluent Technology, Chapter 15

70) Paturau J. M. (1989) "By products of cane sugar industry" , third addition , Elsevier, Amsterdam, The Netherlands.

71) Reeve, D.W. (1996a) "Introduction to the Principles and Practice of Pulp Bleaching", Section 1, Chapter 1 . Tappi Press, Atlanta pp2-24

72) RSAES (1989) Chlorine and chlorine products: Manufacture utilisation and environmental aspects. IVA Report No: 370. Publ. Royal Swedish Academy of Engineering Sciences 44pp

73) Ryan, J.J., Panopio, L.G., and Lewis, D.A. (1988), "Bleaching of pulp and paper as a source of PCDD and PCDF in foods. In DIOXIN '88", The 8th International Symposium on chlorinated Dioxins and Related Compounds, August 21-26. Umea, Sweden.

74) R.Wilson, J.Swaney, D.C. Pryke, C.E.Luthe & B.I.O. Connor, (1992), "Mill operation with chlorine dioxide delignification", Pulp & Paper Canada, 93:10

75) R.A. Sierka & C.w. Bryant, (1994), "Enhancement of biotreatment effluent quality by illuminated titanium dioxide and membrane pretreatment of the kraft extraction waste stream and by increased chlorine dioxide substitution", Water science and technology, Vol. 29 no. 5-6,

76) Ried, A., Mielcke, J., Wieland, A., Schaefer, S., & Sievers, M. (2007), "An overview of the integration of Ozone systems in biological treatment steps", Water sc. Technolo. 55 (12) 253-258

77) Reeve, D.W. & Earl, P.F. (1989), "Chlorinated organic matter in bleached chemical pulp production Part I- Environmental impact and regulation of effluents", Pulp & Paper Canada, 90, No-4, T128-132

78) Reeve, D.W., (1991), "Organochlorine in bleached", Tappi Journal , February ,123-126

79) Riebel, P.N., Owen, M. & Yazer, M., (1997) "Toxicity prevention and response", Pulp & Paper Canada, (5): 23-26

80) Suntio, L.R., Shiu, W.Y. & Mackay, D. (1988) "A review of the nature and properties of chemicals present in pulp mill effluents", Chemosphere 17 (7): 1249-1290

81) Sodergren, A. & Wartiovaara, J. (1988) "Forest Industry Wastewaters- Environmental Effects", Water Science and Technology 20 (2): 210pp.

82) Swanson, S.E., Rappe, C., Malmstrom, J., Kingstad, K.P. (1988), "Emissions of PCDDs and PCDFs from the Pulp Industry", Chemosphere 17, No. 4. pp. 681-961

83) Savant, D., Abdul Rahman, R. & Ranade, D., (2006), "Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry waste water" Bioresource Technology, 1092-1104

84) Stromberg, L. , Morck,R., Filipe de Sousa & Dahlman, O., (1996) "Effects of internal process changes and external treatment of effluent chemistry", Book on Environmental Fate & Effects of Pulp & Paper Mill Effluents, Edited by Mark R. Servos, Kelly R. Munkittrick, John H. Carey, Glen J. Van Der Kraak, 3-20

85) Svard, S.H., Jour,P. Bryant,P.S., Bast, J. and Aggarawal,P. (1999) "Increasing the biotreatability of ECF bleaching effluents by ultrafiltration and partial closure alkaline filtrates", TAPPI International Environmental Conference

86) Saunamaki R., Tokinan K., Jarvinen R., & M.Salvolanian, (1991), "Factors affecting the removal and discharge of organochlorine compounds of activated sludge treatment plant", TAPPI International Environmental Conference , 813-819

87) “Standard methods for the Examination of Water and Wastewater” prepared and published by American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollutional Control Federation (WPCF).

88) S.M.Odendahl, K.M.Weishar & D.W.Reeve, (1990), “Chlorinated organic matter in bleached chemical pulp production: A review of measurement techniques for effluents”, Pulp & Paper Canada, 91:4

89) Smith, T.J., Wearne, R.H. & Wallis, A.F.A. (1994c) “Characteristics of the chlorinated organic substances in filtrates from bleaching of oxygen delignified eucalypt kraft pulp”, Water Science and Technology 29 (5-6): 61-

90) Sierka, R.A. & Bryant, W.C., (1988), “Removal of organic carbon and chlorine from kraft mill wastewater – pretreatment with catalyzed ozone and powered activated carbon”, TAPPI Environmental Conference

91) Svensson, B.G., Nilsson, A., Hansson, M., Rappe, C., Akesson, B. & Skerving, S. (1991) “Exposure to dioxins and dibenzofurans through the consumption of fish.” New England J. Medicine 324: 8-12

92) Training package –2 on determination of acute lethal toxicity of effluent, NIIEM, Phase II, March-(1993)

93) Thompson G, Swain J, Kay M, Forster C.F (2001), The treatment of pulp and paper mill effluent: a review, Bioresource Technology Volume 77, Issue 3, May, 275-286

94) Utne & Hegbom, L. (1992) “Microscopy studies of wheat straw and rice straw for the pulp and paper industry”, Second international non wood pulping conference, Beijing.

95) Voss, R. H, Wearing, J.T, Mortimer R.D, Kovacs T & Wong A, (1980), “Chlorinated Organics in Kraft Bleaching Effluents”, Pap eri Ja Puu 62, 809-814

96) Vidal, G., Becerra, J., Hernandez, V., Decap, J. & Xavier, C. (2007), “Anaerobic biodegradation of sterols contained in Kraft mill effluents”, J. Biosci. Bioeng. 104(6), 476–480.

97) Walden C.C. and Howard, T.E. , (1977) “Toxicity of Pulp and Paper mill effluents – A review of regulation and research”, TAPPI Journal 60 (1): 122-125

98) http://www.iloveindia.com/economy-of-india/paper-industry.html

99) Whittle, D.M., Mageau, C., Duncan, R.K., Sergeant, D.B., Nassichuk, M.D., Morrisson, J. & Piuze, J. (1993) “Canadian national dioxin sampling program: dioxins and furans in biota near 46 pulp and paper mills using the chlorine bleaching process”, Chemosphere 27: 279-286

100) Wagner, J. (1981), “Removal of color COD and toxicity from kraft bleach effluent” APPITA, Vol 36 no.1, 52-55

101) Whittemore, R.C., LaFleur, L.E., Gillespie, W.J., Amendola, G.A., & Helms, J. (1990), “USEPA/Paper industry cooperative dioxin study: the 104 mill study”, Chemosphere 20, No. 10-12. pp. 1625-1632.

102) Wilson, D.G. & Holloran, M.F. (1992), “Decrease of AOX with various external treatments”, Pulp & Paper Canada, 93:2, 372,

103) Wilson, R., . Swaney, J., Pryke, D.C., Luthe C.E. & Connor, B.I.O. (1992), “Mill operation with chlorine dioxide delignification”, Pulp & Paper Canada, 93:10

ABBREVIATION

AOX	:	Adsorbable Organic Halide
EOX	:	Extractable Organic Halide
BOD	:	Biological Oxygen Demand
D.O.	:	Dissolve Oxygen
Conc.	:	Concentrated
TOCl	:	Total Organic Chlorine
COD	:	Chemical Oxygen Demand
TSS	:	Total Suspended Solid
TDS	:	Total Dissolved Solid
TS	:	Total Solid
PCU	:	Platinum Cobalt Unit
mg	:	Milligram
hr	:	Hour
cm	:	Centimeter
mg/l	:	Milligram per liter
ETP	:	Effluent Treatment Plant
C-stage	:	Chlorination stage
E-stage	:	Extraction Stage
H-stage	:	Hypo stage
kg/t	:	Kilogram per ton
% I	:	Percent illumination
ISO	:	International Standards Organisation
TAPPI	:	Technical Association of the Pulp & Paper Industry
APHA		American Public Health Association
AWWA		American Water Works Association

WPCF		Water Pollutional Control Federation
CPPRI	:	Central Pulp & Paper Research Institute
ECF	:	Elemental Chlorine Free
TCF	:	Total Chlorine Free
RCF	:	Recycled Fiber
TCDD	:	Tetra Chloro Dibenzopara Dioxin
PCDF	:	Penta Chloro Dibenzopara Furan
gpl	:	Gram per liter
tpd		Tonne per day
kg/l	:	Kilogram per liter
DBD	:	Dibenzodioxin
DBF	:	Dibenzofuran
MLSS	:	Mixed Liquor Suspended Solid
POP	:	Persistent Organic Pollutants
MW	:	Molecular Weight
ODL	:	Oxygen delignification