REPORT

ON

Detoxification of Bleach Plant Effluent for Recycle and Reuse

Submitted to

Cess Grant Authority

(Development Council for Pulp, Paper & Allied Industries)

By

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BACKGROUND & OBJECTIVE OF THE PROJECT:

The chlorinated phenolic compounds formed during the bleaching of pulp with chlorine based chemicals have long been known to cause toxicity to the aquatic life. The discharge of these chlorinated phenolics became an environmental issue in 1970's when high concentration of these compounds were detected in fish stock receiving bleach plant effluents. The formation of chlorinated phenolic compounds depends primarily on fibrous raw materials, nature and quantity of residual lignin in pulp & bleaching process employed.

The bleaching of pulp with molecular chlorine has become the major environmental concern since it produces a variety of chlorinated phenolics, dioxins and furans that are highly toxic, and have tendency to accumulate and persist in environment for long time. The reduction of these chlorinated phenolic compounds at source involves the adoption of new environmental friendly technologies like extended and oxygen delignification, ECF & TCF bleaching etc. The pulp mills abroad have adopted these new technologies to reduce the levels of chlorinated phenolic compounds below toxicity level. While Indian Pulp & Paper Industry continue to use conventional pulping and bleaching technologies and generates high level of chlorinated phenolic compounds as the scale of operation, use of mixed raw materials and high capital restrict Indian mills to adopt these new technologies.

In the changed scenario of open market economy, increasing environmental awareness & imposition of stringent discharge standards, the Indian pulp and Paper mills are at the cross roads. The immediate alternative/options available are to explore the feasibility of end of pipe treatment methods for treatment of bleach plant effluents to reduce the toxicity to make them suitable for recycling as well as for discharge to the recipient body. The advantages of detoxification of bleach plant effluent are double fold i.e. on one hand it will reduce the pollution load and on other hand it will help in increasing recycling/reuse of bleach plant effluent within the process thus helping the industry in reducing water consumption.

The present studies are aimed to evaluate techno economic feasibility of end of pipe treatment (EOP) methods i.e. physicochemical methods for treatment of bleach plant effluent in order to reduce the pollution load & level of toxicity if it is discharged to the recipient.

INTRODUCTION:

Environmental pollution from pulp and paper industry has been a matter of serious concern. The pulp and paper industry is one of the largest water consuming industry today. During manufacture of pulp and paper large volume of effluents are discharged into the recipient stream. The pulp and Paper Industries are now forced to produce high brightness quality paper for their survival as well as to compete with foreign suppliers. Bleaching to attain high brightness is most effectively achieved with the use of chlorine and chlorine dioxide. The chlorinated phenolic compounds formed during the bleaching of pulp with chlorine based chemicals have long been known to cause toxicity to the aquatic life. The discharge of these chlorinated phenolics became an environmental issue in 1970's when high concentrations of these compounds were detected in fish stock receiving bleach plant effluents. Pulp and paper mill effluents are complex in nature. The characteristics of effluent streams are dependent on numerous factors including raw material usages, process, technology and end product (including washing, cooking, bleaching etc.) as well as final effluent treatment. The increased environmental awareness, adverse effect of chlorinated phenolics, customer preferences for ecofriendly products and imposition of stringent discharge norms forced the pulp mills in developed countries to develop and adopt the environmental ecofriendly technologies to reduce the discharge of chlorinated organic compounds in their mill effluents. As a result the pulp mills in developed countries initiated R&D efforts focusing mainly on the identification of areas for development of technologies so as to reduce the formation of chlorinated organic compounds.

Environmental Impact of chloroorganic compounds:

Among the various effluent stream generated in pulp and paper mill, bleach plant effluent is found to be most toxic .The various compounds present in bleach plant effluent are depicted in **Fig -1**

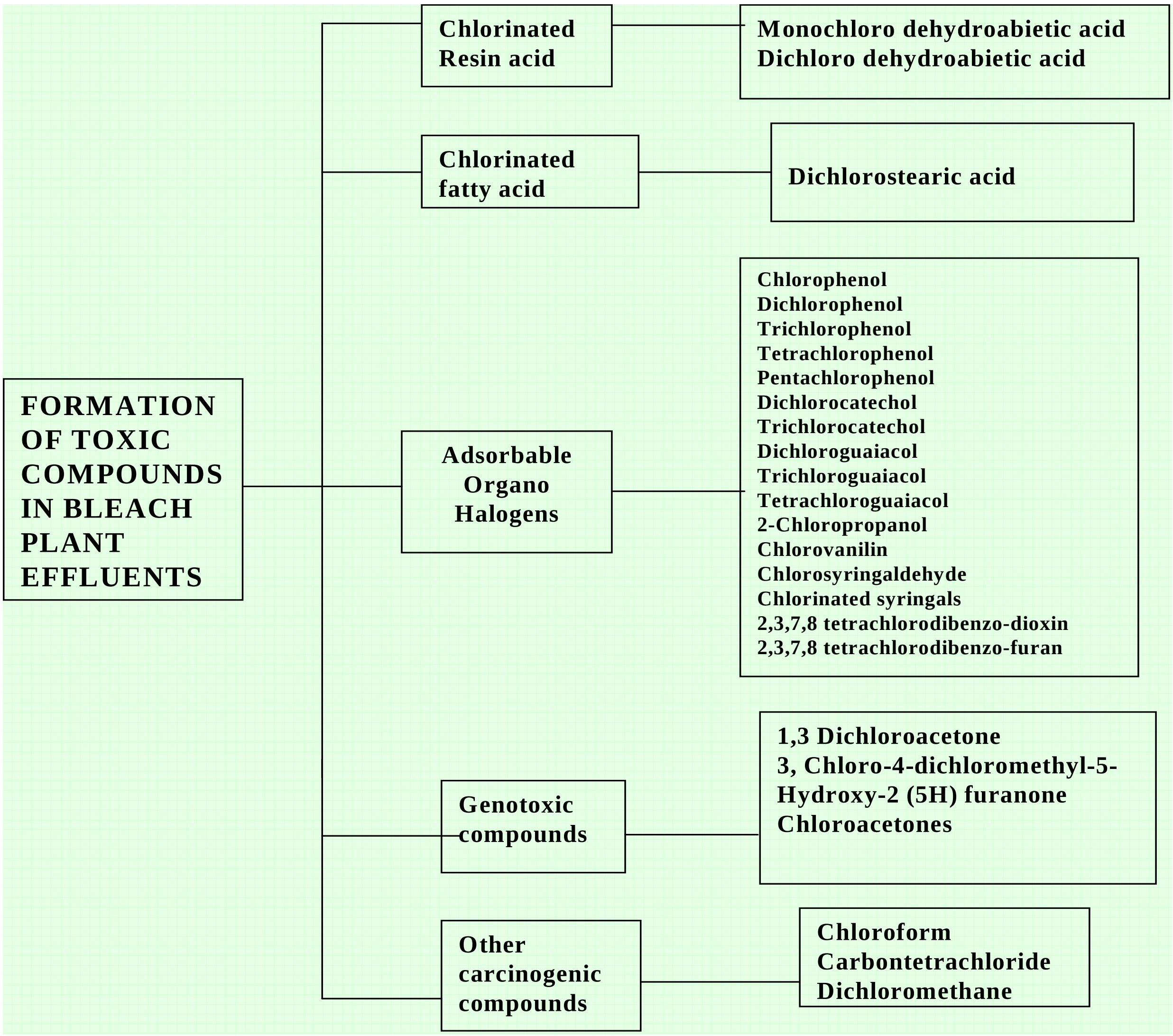


Fig. 1 Various Compounds Present in Bleach Plant Effluents

Earlier the high molar chlorinated, compounds was thought to contribute little or no toxicity to the aquatic organisms due to its large size of molecule. But later on, the studies conducted revealed that high molecular weight chlorolignin accumulated in sediments & over a period of time, these compounds further break down into more biologically active lower molar mass which can cause toxicity to the aquatic life.

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.

Carcinogenic & Mutagenic Compounds.

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. A list of chlorophenolic compounds generated during the chlorine based bleaching are indicated in **Table –2**

Table –2

Chlorinated Phenolic Compounds Generated During Bleaching of Pulp with Chlorine Based Chemicals

Type		**Amounts**
Chlorinated acids	40	Upto 500g/t pulp
Chlorinated phenolics	40	Upto 100g/t pulp
Chlorinated aldehydes, Ketone and lactones	45	---
Chlorinated hydrocarbons	45	----
Chlorinated others	20	----
High molecular weight Materials	--	Upto 4kg.Cl/t pulp

Polychlorinated Dioxins & Furans:

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. The list of POP (commonly called as dirty dozen) is given in **Table – 3**

Table-3

List of Dirty Dozen Persistent Toxic Pollutants (POP) (Stockholm Convention)

Compounds	Source
Aldrin	Pesticide
Chlordane	Pesticide
DDT	Pesticide
Dieldrin	Pesticide
Endrin	Pesticide
Heptachlor	Pesticide
HCB	Pesticide
Mirex	Pesticide
Toxaphene	Pesticide
PCBs	Industrial
Dioxins	**By-product**
Furans	**By-Product**

Some other interesting facts about dioxins are summarized below:

- There is no known use for dioxins
- Dioxin is slow to break down and can last for long period.
- Animals consume dioxin-contaminated water and plants and then these dioxins accumulates in their fat.
- People are exposed to dioxin through eating food high in fat, like dairy products and beef.
- Dioxin can be transmitted from mother to child during pregnancy and nursing.
- The preliminary studies conducted on toxicity of dioxins on humans yielded contradictory findings. However, recently it has been accepted that dioxins even in trace amounts may cause a wide range of other adverse effects on human health.

Some of them are listed below:

Low-exposure effects:

- Altered immune function.
- Increased susceptibility to infections, and
- Thyroid and liver function abnormalities.

Higher levels of dioxin exposure:

- Birth defects.
- Child growth retardation,
- Reduced levels of male reproductive hormones,
- Diabetes, and cancer

Human carcinogen:

Dioxins are classified by the International Agency for Research on Cancer as a known human carcinogen.

Though the level of dioxins is less than 0.1% (of total AOX) but these compounds are reported to be highly lypophyllic and bioaccumulable compounds. As such there is no safe level of dioxins. Such compounds are formed when unchlorinated dibenzodioxin **(DBD)** and dibenzofuran **(DBF)** present in unbleached pulp are chlorinated with elemental chlorine in chlorination stage. The oil based pulp mill additives particularly brown stock defoamers have been identified as potential sources of such compounds. Laboratory studies indicate a sharp increase in quantity of PCDD & PCDF when elemental chlorine consumption increased beyond 10-15 kg /t pulp. The toxicity level of dioxins in various countries are given in **Table -4**

Table -4
Toxicity levels of dioxin

Agency/Country	Risk dose	Toxic/health effect
EPA	6.4×10^{-3} *	Cancer
Germany	1.0*	Cancer/reproductive
Netherlands	4.0*	Cancer
Switzerland	A**	
FDA	5.7×10^{-2}	Cancer

*Pico grams of 2,3,7,8 TCDD per Kg. Of body weight per day.
**(A) the studies have not established the safety levels.

TECHNOLOGICAL DEVELOPMENTS TO REDUCE AOX LEVEL:

Pulping and bleaching are the thrust areas where remarkable developments have taken place in the last two decades which have reduced the overall environmental impact (including AOX) associated with pulp and paper industry. In recent years the trend in technology developments have been:

- Extended delignification (Modified batch pulping process)
- Oxygen delignification
- Development of Elemental chlorine free (ECF) and Total Chlorine free (TCF)
  Bleaching techniques.
- Introduction of oxidative alkali extraction stage in bleaching.
- Biotechnological applications - Biopulping & biobleaching.
- Use of high yield pulps in cultural papers.
- Use of recycled fiber

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

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.

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.

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 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.

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 made in the development of these techniques.Thus most of pulp mills abroad have switched over to the elemental chlorine (Cl_2) 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 in **Table 5.**

Table 5
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	

However, the chlorine dioxide is still the dominating bleaching chemical preferred by industry to achieve high brightness. **Fig.- 2** shows the changes in pulping concepts from 1970-2000 in developed countries, which indicates gradual increase in extended cooking stage, while there is shrinkage of bleaching profile.

The development in pulping process as shown in **Fig.- 2** indicates that the adoption of combination of modified cooking and oxygen delignification processes have reduced the kappa no. of pulp from 35 in 1970 to 10 in early 1990. Efforts are still continued to reduce kappa no. of pulp below 10. These measures have resulted in reduction of **AOX** i.e. Absorbable Organic Halides (a measure of the amount of chlorine bonded with organic matter) from 6-8 kg to below 2 kg per ton of pulp in 1990's .

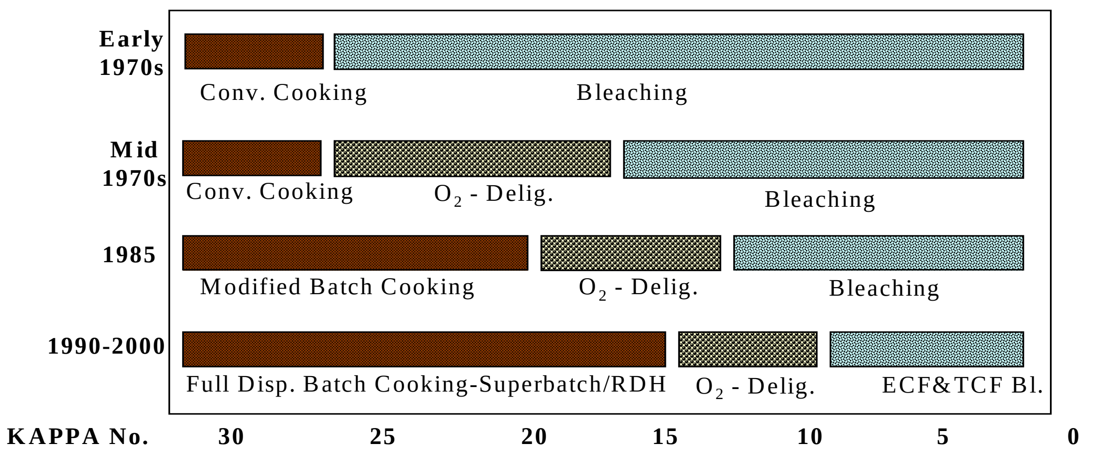


Fig. 2 Developments in Pulping and Bleaching Process

Oxidative Alkali Extraction Bleaching

The adoption of peroxide / oxygen reinforced alkali extraction stage is also an increasing trend in pulp and paper mills to improve the quality of pulp and bleach plant effluent. The addition of oxygen or peroxide in alkali stage bleaching improves the brightness of pulp and also the quality of bleach plant effluent by reducing color, COD & AOX. The pulp mills abroad and also in India particularly large paper mills have already employed the oxidative alkali extraction bleaching and most of them are using hydrogen peroxide in extraction stage of bleaching to improve the quality of pulp and effluents. **Table- 6** clearly shows the advantage of use of peroxide in oxidative alkali extraction in bleaching.

Table – 6
Effect of H_2O_2 enhanced process on chlorinated organics

Parameters	**Without H_2O_2**	**With H_2O_2**
2,3,7,8- TCDD in pulp, pg/ODg.	4.8	Not analysed
2,3,7,8- TCDF in pulp, pg/ODg.	49.0	1.3
AOX in untreated effluent, Kg./t	4.2	3.1

Technological Status of Indian Pulp & Paper Mills:

The pulp and paper industries in India are scattered, old and vary in terms of size, use of fibrous raw material , process employed , machinery used and end products. These mills use a wide range of fibrous raw materials to produce variety of paper. In view of AOX discharge the paper mills are categorised broadly into:

- Large Scale Mills (with chemical recovery process)
- Small Scale Mills (without chemical recovery process)

The technological status of these mills is discussed below:

Scale of Operation:

The scale of operation in large scale pulp and paper mills ranges from 100-275 tonnes of pulp per day which in small mills is in range from 20-70 tonnes pulp per day. The low scale of operation of Indian paper mills is primarily due to scarcity of wood and inconsistent supply of other forest based raw materials. Further, the resource constraint is another reason for low scale of operation. Almost all the small scale mills are operating without chemical recovery system because of size constraint and are discharging their black liquor along with other waste water.

Level of Technology:

Pulping process:

The kappa number of the unbleached pulp produced in large mills varies between 18-26. The reason for maintaining high kappa are the mixed raw material pulping and capacity limitation of chemical recovery boiler. By the same process the integrated agro residue based mills are producing pulp of kappa number between 14-16. J.K. Paper Mills, Orissa is the only mill employing modified RDH pulping process and oxygen delignification process i.e. advanced pulping technologies to produce pulp of better quality and low kappa number between 12-14 by using bamboo and eucalyptus. Almost all the small scale agro based mills are employing soda pulping for producing pulp of high kappa number i.e 30-32 due to economic reasons as conventional chemical recovery system is not practiced and major part of lignin is removed in subsequent conventional bleaching process using elemental chlorine and hypochlorite .

Pulp washing system

The large integrated mills normally use conventional brown stock washers **(BSW)** with counter current washing for extraction of black liquor and washing of pulp. The efficiency of BSW's is defined in terms of soda losses and carry over of organic matter along with pulp entering the bleaching section. Due to inherent quality of fibers in the pulp from these raw materials and washing technology employed, the carryover of the organic matter, in terms of COD is generally on higher side. The washing efficiency of existing BSW's operating in small mills are even more lower as 50-70% higher carry over of COD along with pulp compared to large wood based mills has been observed which results in increase of demand of bleaching chemicals.

Bleaching process:

Most of the large integrated mills are using conventional CEHH sequence for bleaching of pulps to a brightness level of 80-85% ISO , primarily to produce quality products of international standards. Some mills have started the use of chlorine dioxide along with elemental chlorine during chlorination and in final stages of bleaching only to get higher and stable brightness of pulp. The consumption of total chlorine in these mills varies from 60-100 kg/ t_{pulp}. Most of these pulp mills are now using oxidative alkali extraction bleaching to increase pulp brightness and improve the quality of pulp and bleach plant effluent. The small scale mills based on agro residues also use conventional CEHH/ HH sequence to bleach the pulp to a brightness level of 75-80%. The consumption of chlorine in these mills is comparatively high and varies 140-160 kg/t_{pulp} primarily because of high kappa number of unbleached pulp and also high carry over of COD along with unbleached pulp.

The pulp mills in developed countries have incorporated various measures to changeover to new fiber line in pulp mills which includes extended delignification, improved pulp washing, oxygen delignification , chlorine dioxide bleaching etc. However, the application of this technological development is mostly limited to developed countries primarily due to advantages of consistent supply of wood based fibrous raw materials and high capacity of pulp mills. The use of mixed fibrous raw materials, low scale of operation, high capital investment are the major constraints, which restrict Indian pulp and paper mills to switch over to new cleaner production fiber line.

TECHNOLOGICAL DEVELOPMENTS TO REDUCE AOX LEVEL:

CPPRI has conducted an extensive study to assess the status of technology and level of AOX released in both large and small scale pulp and paper mills producing bleached variety of paper Indian pulp & paper industry. The study shows that the chlorine consumption varies from 35 to 110 kg./t $_{pulp}$ in large mills and 140 to 160 kg/t $_{pulp}$ in small agro based mills. Consequently the AOX generation is also high and varies from 2.0 to 5.3 kg/t $_{pulp}$ in large mills and 6.0 to 10 kg/t paper in small mills. Low level of AOX was observed in the mills using RDH, oxygen delignification and chlorine dioxide bleaching as compared to mills using conventional CEHH bleaching process. In small scale mills the scenario of AOX discharge is more alarming as these mills are using high dosage of chlorine to bleach pulp of high kappa number due to economical reasons. The level of AOX generated and discharged are given in **Table - 7** & indicated in **Fig. - 3 & 4.**

Table-7
Status of AOX in Indian pulp and paper mills

Type of product	Kappa No.	COD Carry over during washing kg. COD / t_{pulp}	Consumption of Cl_2 kg. COD / t_{pulp}	AOX Level, Kg./t $_{Paper}$	
				Generated	Final discharge
Rayon grade Pulp	12 - 16	Kappa No. Differ 1.5 units	25 - 28	0.7-1.0	0.50
News print chemical pulp	20 - 22	--	20 - 25	0.50- 0.60	0.50
Writing & Printing Paper: -Large Mills	15 - 26	20 – 25	35 – 80	1.90 - 5.30	1.0- 2.70
- Small Mills (Agro-based)	15 - 50	30 – 40	100 - 150		3.0- 6.5

The low level of AOX in the newsprint & rayon grade mills is primarily due to low kappa no. of pulp, use of chlorine dioxide for bleaching of rayon grade pulp and use of high proportion of mechanical pulp bleached with hydrogen peroxide in newsprint production.

The problem of AOX is more acute in writing and printing paper mills where AOX level varied from 2.0-5.3 kg/t of paper in large mills and 6-10 kg /t of paper in small agro based mills.

Fig –3

Level of AOX generated in Indian Pulp & Paper Mills

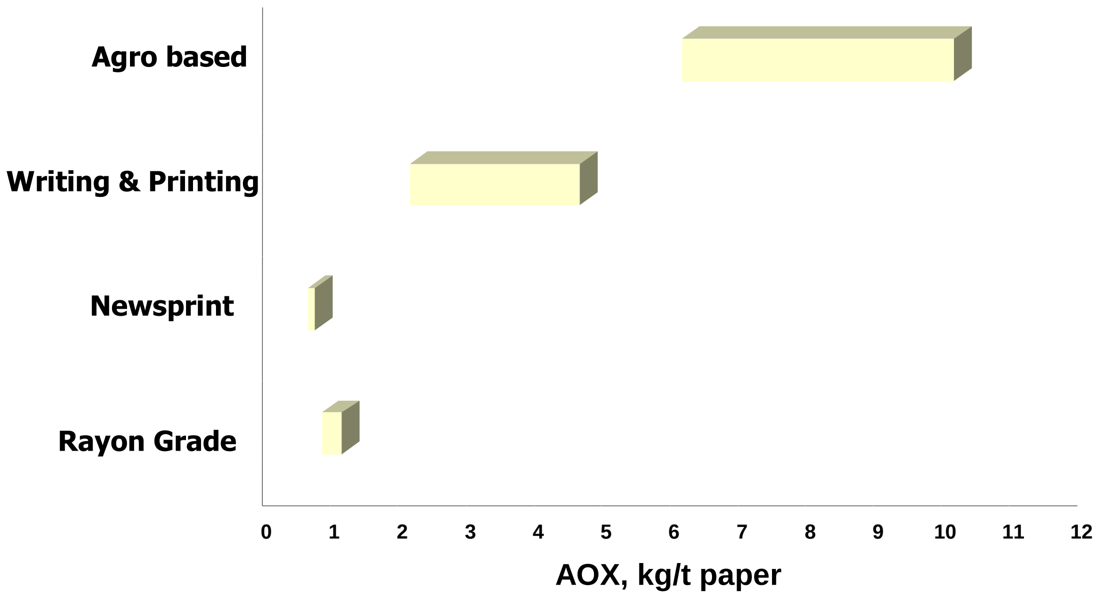
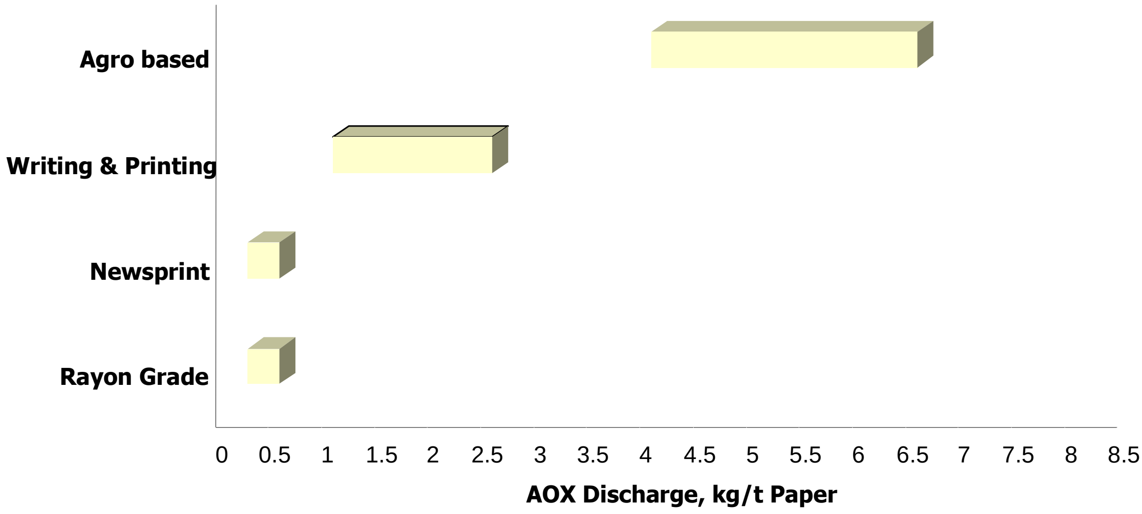


Fig –4

Level of AOX discharged in Indian Pulp & Paper Mills



The high value of AOX in writing and printing mills is primarily due to:

- Use of mixed fibrous raw materials.
- High kappa no. of pulp ranging from 20-26.
- High carryover of organic matter along with pulp to bleach plant.
- Use of high proportion /dosage of elemental chlorine.
- Obsolescence in technologies.

The level of AOX in writing and printing paper mills is in general high compared to the paper mills of the developed countries. The lower value of AOX has been observed to be in mills which employ modern pulping and bleaching process. A comparison of the Indian paper industry and that of developed countries is given in **Table- 8**

Table- 8

A comparative status of paper mills in India & developed countries

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

Constraints in Adoption of Modified Pulping & Bleaching Technologies by Indian Mills:

The application of the new modified pulping and bleaching technologies have been limited to the developed countries primarily due to consistent supply of uniform fibrous raw materials & higher 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 150-600 t/d in large mills and 5-100t/d in small mills.

Similarly in case of ECF bleaching technologies one of the main requirements 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. The comparative techno-economic analysis of the new pulping and bleaching methods discussed above are summarized in **Table -9**

Table – 9

Comparative Techno-Economic Analysis of New Pulping & Bleaching Process in Indian Perspective

Technologies	Minimum Investment Rs. crore	Level of Operation t/d	Limitations
Extended Delignification	55-60	350	Low level of operation Use of mixed fibrous raw materials
Oxygen Delignification	20-25	300	High capital investment
Chlorine dioxide bleaching (2.0-2.5 t/d)	32-35	300	Age of mills Require new infrastructure

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. M/s J.K. Paper Mills has already switched over to new fiber line involving RDH pulping, oxygen delignification and chlorine dioxide bleaching. M/s ITC Paper & Boards, Bhadrachalam has recently switched over to new fiber line. Some more mills are also planning to go far such new fiber line. Few Indian mills have also started the use of chlorine dioxide in chlorination stage along with elemental chlorine and also in the final stage of bleaching, to get a stable and high brightness level. However, the elemental chlorine and hypochlorite are still the dominating bleaching chemicals used in Indian mills. In recent times the trend has been of increased use of recycled fiber in the fiber furnish so as to conserve the virgin fiber as well as reduce the environmental impact by less use of bleaching chemicals.

EMERGING ENVIRONMENTAL ISSUES:

With the introduction of ***Charter on Corporate Responsibility for Environmental Protection (CREP)*** by Central Pollution Control Board, the reduction in AOX levels in the effluent has become a top agenda before Indian Pulp & Paper mills producing bleached variety of papers. The Charter proposes a time bound implementation schedule for reduction in AOX level as under:

Mill category	**Implementation Schedule**
Large Paper Mills	AOX 1.5 kg/ t_{paper} within 2 years AOX 1.0 kg/ t_{paper} in 5 years
Small Paper Mills	Either achieve the discharge Standarsd of BOD, COD & AOX by installation of chemical recovery system or utilization of black liquor with no discharge from pulp mill within 3 years or shift to waste paper Upgrade the ETP within one year so as to achieve the discharge standards

TECHNICAL PROGRAMME:

- Literature Survey
- Characterization of bleach plant effluent from individual bleaching stage and combined bleach plant effluents for various pollutional parameters.
- Optimization of chemical methods for removal of toxic materials.
- Identification of chlorinated phenolic compounds present in bleach plant effluent.
- Evaluation of biological treatment methods for removal of toxic material from treated and untreated bleach plant effluent.
- Evaluation of toxicity level of treated and untreated bleach plant effluent to the aquatic organisms.
- Chemical behaviour of low and high molecular weight chlorinated phenolic compounds
- Evaluation of efficiency and viability of physical methods for removal of toxic material and inorganic chlorides etc. by employing membrane filtration and reverse osmosis techniques and their safe disposal.
- Explore the possibility of recycling / reuse of treated bleach plant effluent to the process.

METHODOLOGY ADOPTED:

Based on the literature survey efforts were made to standardize the method of extraction and identification of different chlorophenolic compounds with gas chromatograph using standard compounds.

Two mills one wood based and one agro based mills were visited to collect individual bleaching stage and combined bleach plant effluents for in depth studies.

The studies on evaluation of chemical methods, optimization of dosages of various chemicals & their combination for the treatment of bleach plant effluents were carried out.

Evaluation of biological treatment methods for removal of toxic material from treated and untreated bleach plant effluent were carried out. Fractionation & mass balance of AOX was determined using membrane of different cut-off values like 1,000, 3,000, 10,000, 30,000 & 100,000 D.

Toxicity studies of treated and untreated bleach plant effluents were carried out using Fish and luminescent bacteria.

Physical treatment methods like Electrofloculation, Carbon Adsorption & Heat treatment studies were also carried out to evaluate the treatment efficiency of bleach plant effluents.

LABORATORY STUDIES FOR TREATMENT OF BLEACH PLANT EFFLUENT:

Indian Pulp & Paper Industry – A Brief Overview:

The Indian pulp and paper industry can be categorized on the basis of production capacity, raw material used as well as end products. On the basis of production capacity the mills are categorized into:

- Large scale (above 100 tpd)
- Medium (50-100 tpd)
- Small (below 50 tpd)

On the basis of raw material used it is classified into:

- Wood based
- Agro based
- Recycled fiber based

On the basis of end products produced it is classified as:

- Writing & Printing
- Newsprint
- Rayon grade

The large scale mills use mostly woody raw materials. Some mills also use agro residues and recycled fiber. Small agro based mill use mixed raw materials which include agro residues as well as recycled fiber depending upon the product requirement. Most of the large scale pulp and paper mills use kraft process while the small mills use the conventional soda process. The kappa number of pulp varies between 15-22 in large scale mills and 25-32 in small scale mills which results in higher consumption of bleaching chemicals (mostly elemental chlorine) in bleaching stage leading to generation of high level of AOX. Less than 5% of the organic halogen emissions from bleaching of pulp are molecules of known structure. The major part consist of mainly hydrophilic molecules of unknown structure, chlorohumus and assumed of high molecular weight 10,000D to 10,000,00D, often called chlorolignin. Chlorolignins are recognized as slow biodegradable and considered humus-like is not being bioavailable, which would explain their recalcitrance.

Characterization of bleach plant effluent:

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, bamboo and eucalyptus. All these three raw material were cooked separately in 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 - 10**

Table-10
Characterisation of bleach effluent (CEH)

Raw materials	COD kg/t $_{pulp}$	BOD kg/t $_{pulp}$	AOX kg/t $_{pulp}$

The pulp obtained above were also bleached by modified bleaching sequences using oxygen and chlorine dioxide to achieve the brightness level of around 80% ISO . Oxygen treatment was carried out under following conditions followed by washing:

Pulp consistency	-	10%
Sodium hydroxide	-	2% for bamboo & eucalyptus 1.2% for bagasse.
Oxygen pressure	-	5 kg/cm^2
Treatment temperature	-	120 ºC
Treatment time	-	30 min.

The characteristics of the bleach effluents thus generated are indicated in **Table -11.**

Table-11

Characteristics of OCEH, OD/CEHD, ODE/HD bleached effluents

Bleaching sequence	COD kg/t $_{pulp}$	BOD kg/t $_{pulp}$	AOX kg/t $_{pulp}$
OCEH			
Baggase	20.4	8.8	0.86
Bamboo	19.8	6.3	1.32
Eucalyptus	16.3	4.8	1.27
OD/CE/HD			
Baggase	18.1	7.2	0.6
Bamboo	17.8	3.3	0.88
Eucalyptus	13.1	2.4	0.83
ODE/HD			
Baggase	15.9	6.9	0.31
Bamboo	11.9	2.25	0.44
Eucalyptus	9.9	1.6	0.40

The study revealed that:

The formation of AOX is directly proportional to the chlorine applied and the level of AOX varies between 2.93 to 4.63 kg AOX/t_{pulp} in different raw materials. The level of chloro-organics as AOX generated is in order of bamboo <eucalyptus < bagasse.

Considerable reduction in AOX was observed by adopting modified bleaching sequences

Change of the bleaching sequence from CEH to ODE_OD, resulted in the reduction of AOX ~90% in all the raw materials studied

Bleach plant effluents collected from agro based and a wood based mills using chlorine based conventional bleaching sequences were characterized for various pollutional parameters including AOX **Table –12 &13.**

Table –12
Characterization of Bleached Plant Effluent collected from agro based mill

Parameters	C-stage	E-stage	H_1-stage	Combine bleach effluent
PH	2.5	10.2	7.1	7.8
COD mg/l	971.96	1488.96	1985.28	1158.08
BOD_3 mg/l	225	310	808	402
T.S. mg/l	1602	2320	4309	2162
T.S.S., mg/l	183	201	180	230
T.D.S., mg/l	1419	2119	4129	1932
Colour, PCU	136	3760	152	1310
AOX (mg/l)	70.39	75.95	47.70	54.97
Lignin, mg/l	97.11	505.3	72.0	232.6
Chloride (mg/l)	749.77	339.89	1437.05	562.33
Organic, (mg/l)%	53.5	45.6	47.8	46.0
Inorganic, (mg/l)%	46.5	54.4	52.2	54.0

Table –13
Characterization of Bleached Plant Effluent collected from wood based mill

Parameters	C-stage	E-stage	H_1-stage	Combine bleach effluent
pH	2.5	7.0	6.6	5.0
T.S. , mg/l	3200	3460	6940	2970
T.D.S., mg/l	1470	3430	6820	2900
T.S.S., mg/l	1789	40	110	181
COD mg/l	490	1598	1020	1411
BOD mg/l	160	391	350	414
Chloride mg/l	759	766	2537	1089
Color, PCU	305	3460	424	2750
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	70.5	50.7

Detoxification of Bleach Plant Effluent:

In accordance with the work plan the detoxification studies were carried out with a two way approach .i.e.

Chemical treatment methods (Precipitation, Coagulation, Oxidation etc.)

Physical treatment methods (Electrofloculation, Membrane filtration Adsorption and Heat Treatment)

Chemical Treatment Studies:

The studies were focused mainly to optimize the dosages, treatment conditions, combination of chemicals to reduce the level of toxic material in bleach plant effluent. The various chemicals generally used by industry were tried individually & in combination to evaluate their response in reducing the chlorinated phenolic compounds. The response of various chemicals used for treatment of bleach plant effluent are tabulated in Table–14&15 and depicted in Fig -5&6. The results indicate that chemical treatment is quite effective and the reduction in COD, AOX and colour achieved was 50-80%, 50- 81% and 83-97% respectively.

The preliminary economics of the chemical treatment indicates that the cost of treatment of C, E & combined bleach effluent of wood based mill is approximately Rs. 150-200 / t_{pulp}, Rs 250-350 / t_{pulp} & Rs 300-450 / t_{pulp} respectively while in case of agro based mill it is around Rs. 250- 400 / t_{pulp} , Rs 150-350 / t_{pulp} & Rs 400- 650 / t_{pulp} respectively.

TABLE-14
CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(AGRO BASED MILL)

Parameters	C-stage effluent	E-stage effluent	Combined bleach plant effluent
(A) Effluent Characteristics			
pH	1.8	7.1	6.6
COD mg/l	3528	2307	2883
AOX mg/l	48.2	125.3	50.02
colour, PCU	3372	6778	3689
(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)	-	2.0	2.0
(C) Treated Effluent Characteristics			
pH	5.5	5.6	5.0
COD mg/l	1033	438	542
AOX mg/l	23.82	62.2	21.06
colour, PCU	145	246	156
(D) Removal Efficiency, %			
COD	71	81	81
AOX	51	50	57
Colour	95	96	96

TABLE-15
CHEMICAL TREATMENT OF BLEACHED PLANT EFFLUENT
(WOOD BASED MILL)

Parameters	C-stage effluent	E-stage effluent	Combined bleach plant effluent
(A) Effluent Characteristics			
pH	**2.0**	**9.0**	**6.4**
COD mg/l	**851**	**3048**	**612**
AOX mg/l	**46.16**	**134.0**	**37.8**
colour, PCU	**392**	**11320**	**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**	**10.0**	**2.0**
(C) Treated Effluent			
Characteristics	**5.5**	**5.5**	**5.5**
pH	**240**	**596**	**306**
COD mg/l	**18.14**	**25.43**	**13.23**
AOX mg/l	**67.0**	**363**	**61.0**
colour, PCU			
(D) Removal Efficiency, %			
COD	**72**	**80**	**50**
AOX	**61**	**81**	**65**
Colour **,** PCU	**83**	**97**	**94**

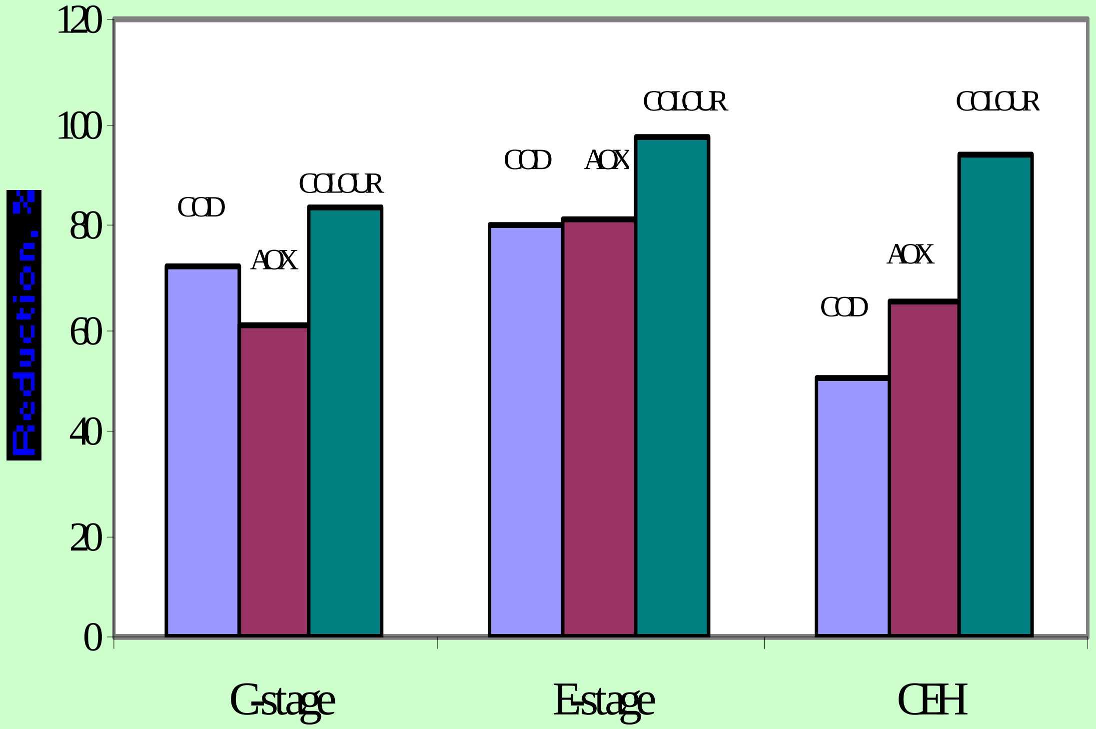


Fig. 5 Chemical Treatment of Bleach plant effluent collected from wood based mill

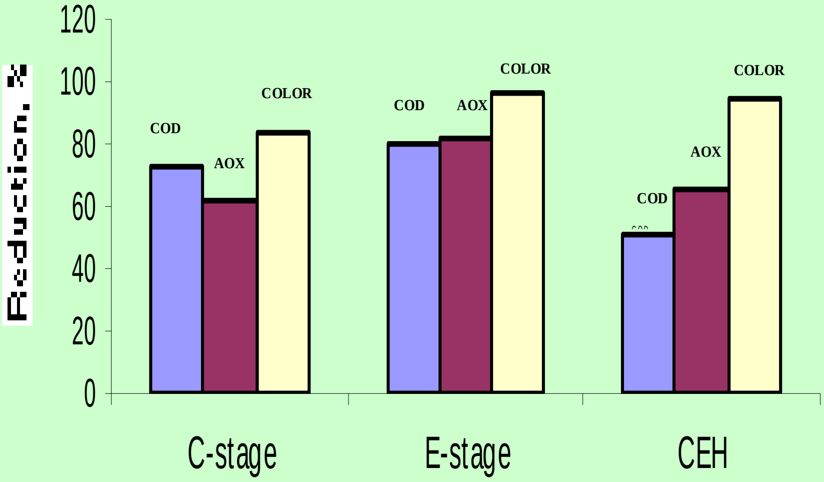


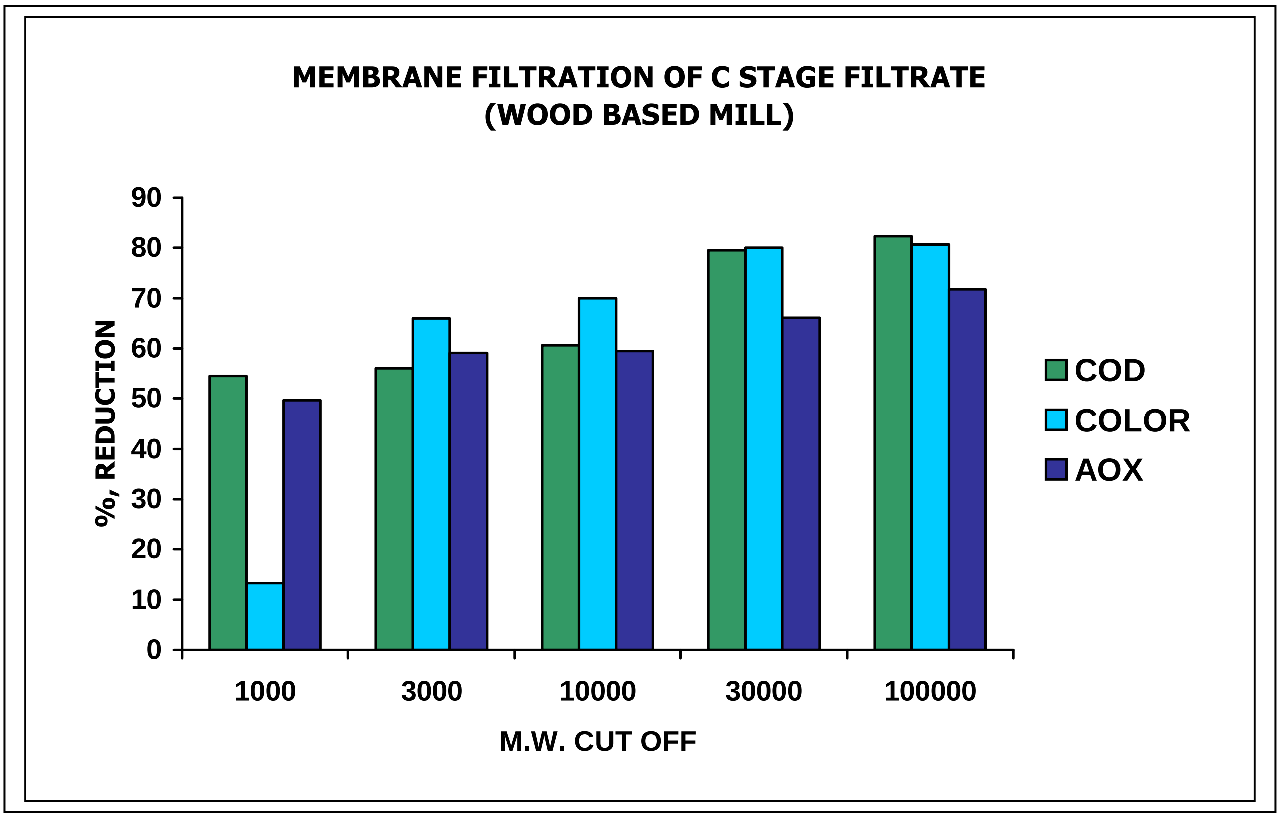
Fig. 6. Chemical Treatment of Bleach Plant Effluent collected from Agro based mill

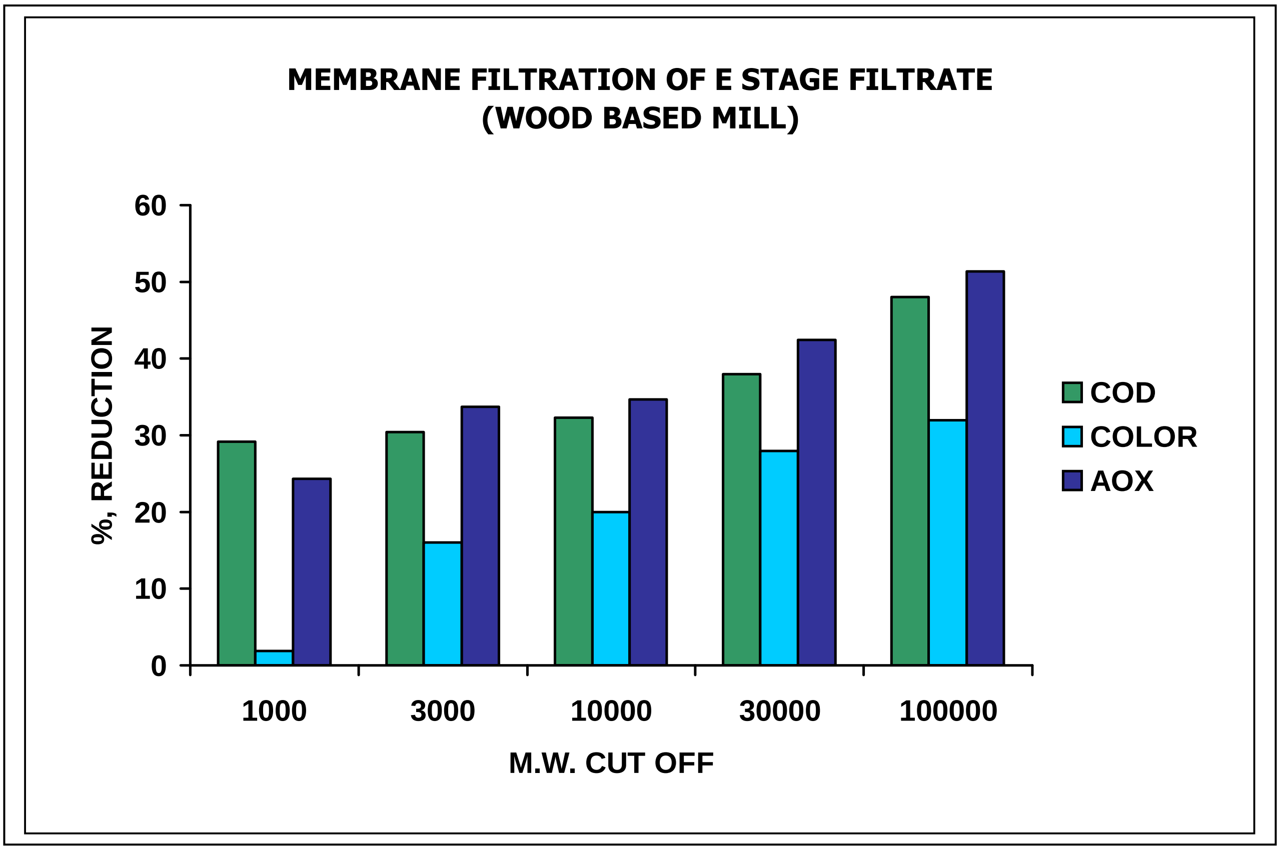
Physical Treatment Methods:

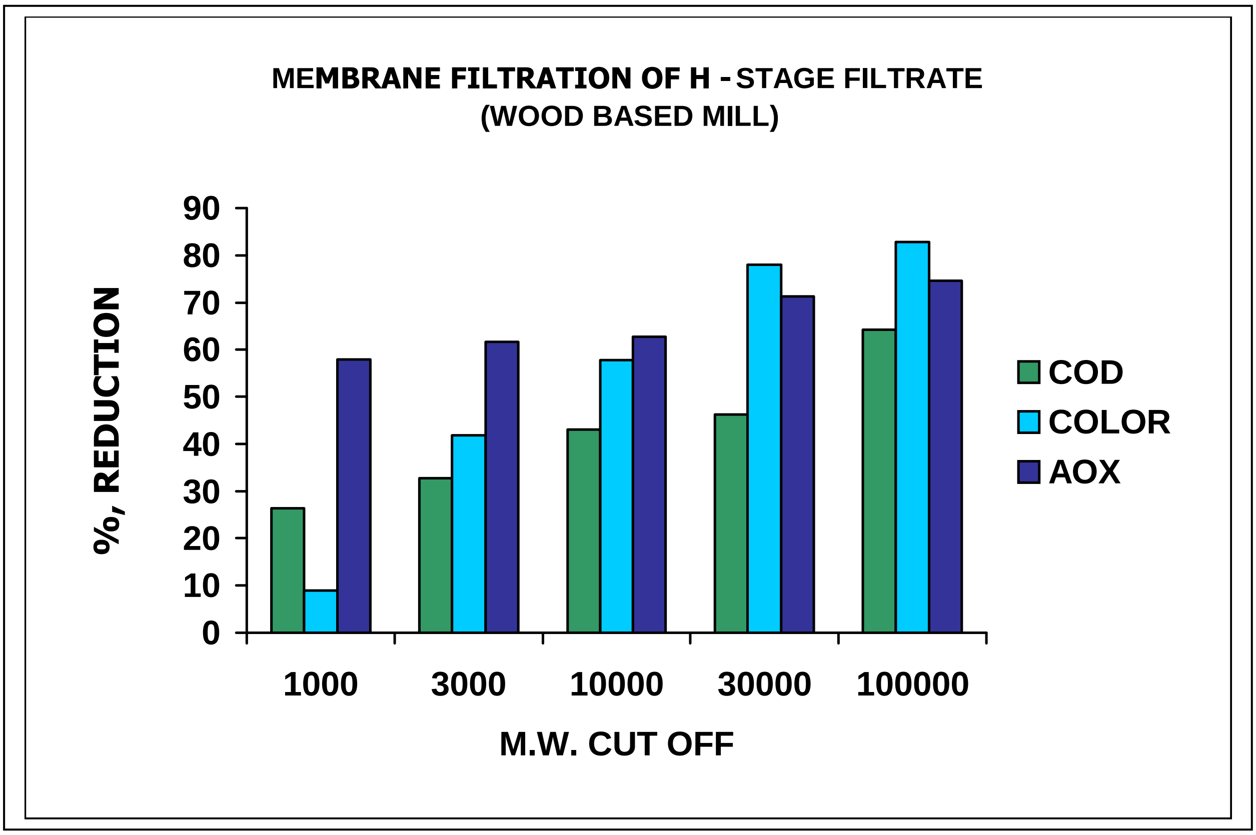
Membrane Filtration:

In a membrane process feed water is hydraulically pressurized by a pump or air and passed across a membrane in a “cross flow” direction. The feed water is divided into a product or permeate which, together with some inorganic and organic molecules, transports through the membrane while the remainder of the influent waste water, termed the concentrate stream, conveys the materials rejected at the membrane surface from the module. The degree of pollutant separation is controlled by the selected membrane chemistry and manufacturing method. Rejection is enhanced by a “tighter” membrane, which is related to pore size. Conversely permeate productivity is reduced as pore size decreases.

The bleach plant effluents (C-stage, E-stage, H-stage & combined) collected from wood and agro based mills were fractionated into various fraction using membranes of different cut-off values like 1,000 , 3,000 , 10,000 , 30,000 and 100,000 D at a volume reduction factor (VRF) of five (5). The VRF is defined as the initial feed water volume divided by instantaneous concentrate volume. The permeate collected were analyzed for COD, colour and AOX reduction. The results obtained are summarized in Fig. 7, 8, 9 &10. The aim of the membrane filtration was to evaluate the proportion of different AOX related fractions in order make the mass balance of AOX related chloroorganic compounds present in the bleach effluent. The permeate and concentrate obtained were analyzed for various pollutional parameters including toxicity and AOX. The mass balance of AOX in different bleach plant effluent is indicated in Fig. 11&12.


MEMBRANE FILTRATION OF C STAGE FILTRATE
(WOOD BASED MILL)
%, REDUCTION
90
80
70
60
50
40
30
20
10
0
1000
3000
10000
30000
100000
M.W. CUT OFF
COD
COLOR
AOX


MEMBRANE FILTRATION OF E STAGE FILTRATE
(WOOD BASED MILL)
%, REDUCTION
60
50
40
30
20
10
0
1000
3000
10000
30000
100000
M.W. CUT OFF
COD
COLOR
AOX


MEMBRANE FILTRATION OF H - STAGE FILTRATE
(WOOD BASED MILL)
%, REDUCTION
90
80
70
60
50
40
30
20
10
0
1000
3000
10000
30000
100000
M.W. CUT OFF
COD
COLOR
AOX

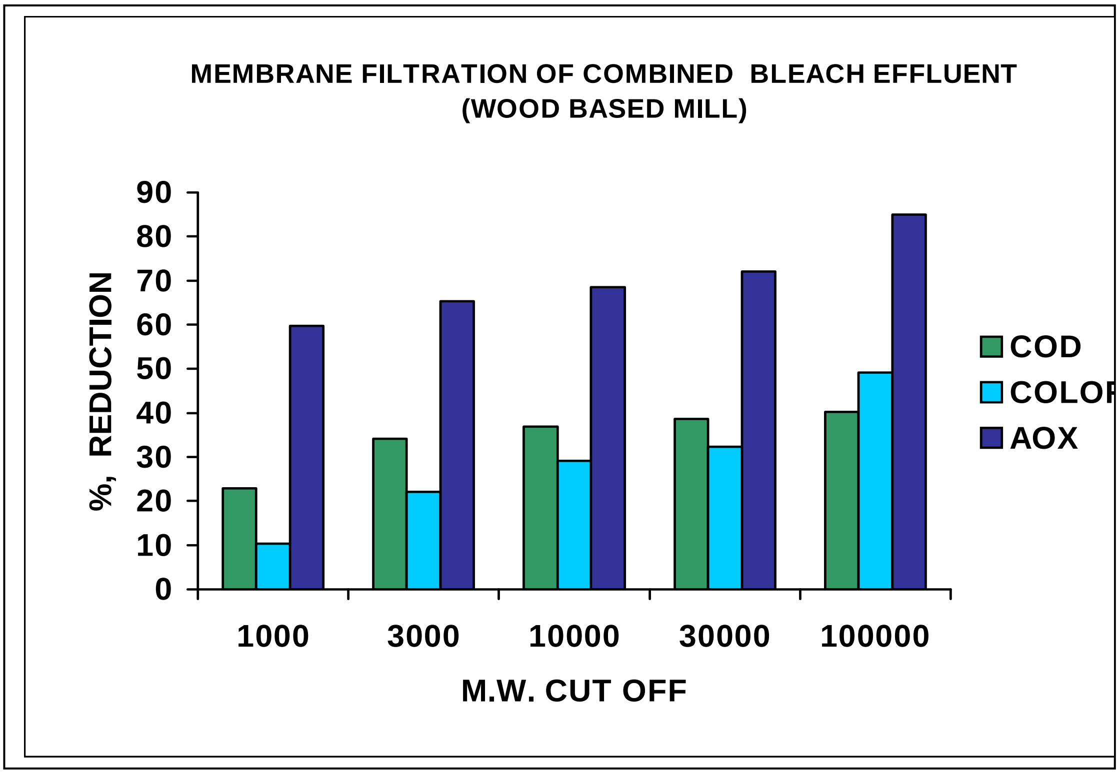

MEMBRANE FILTRATION OF COMBINED BLEACH EFFLUENT
(WOOD BASED MILL)
%, REDUCTION
90
80
70
60
50
40
30
20
10
0
1000
3000
10000
30000
100000
M.W. CUT OFF
COD
AOX

Fig. 11 Mass Balance of Combined Bleach Effluent using different MW Cut off Filters. (Agro Based Mill)

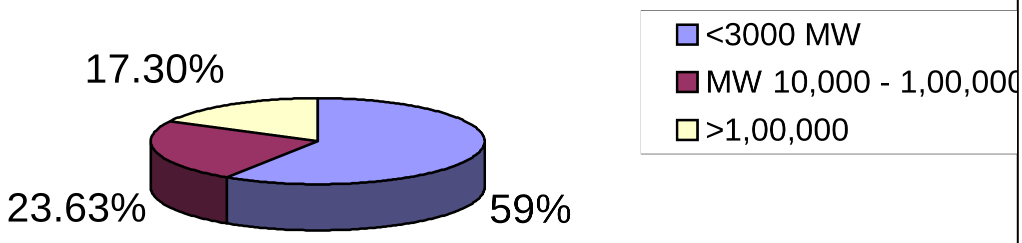
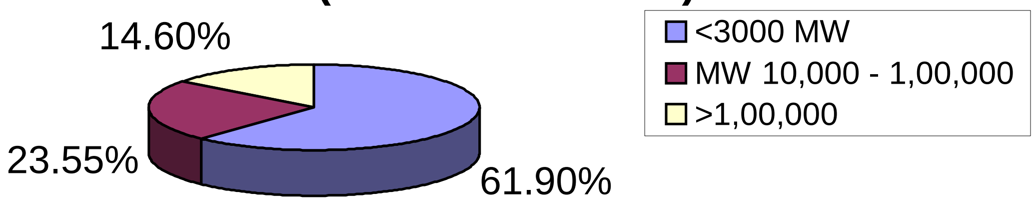


Fig. 12 Mass Balance of Combined Bleach Effluent using different MW Cut off Filters. (Wood Based Mill)



Electrofloculation:

The main advantage of Electrofloculation technique is easy and effective separation of lignin is obtained at very lower input of electric current Electrofloculation studies were carried out in a lab-fabricated electrolytic cell.

The results are indicated in **Table 14 & 15** and depicted in **Fig. 13 to 18**. The preliminary laboratory results obtained are found encouraging. However, studies are continued to evaluate the efficiency and economy at pilot scale for treatment of mill effluent.

TABLE –14

Electrofloculation Studies with Bleach Plant Effluent of an Agro based mill

Parameters	**C- stage**			**E- stage**			` **Combined Bleach Effluent**		
	As such	After treatment	% reduction	As such	After treatment	% reduction	As such	After treatment	% reduction
COD, mg/l	972	114	88.3	1489	102	93.1	1158	69.4	94.0
Colour, PCU	136	42	69.1	3760	102	97.3	1310	38	97.0
AOX, mg/l	70.4	8.5	87.9	76.0	8.0	89.5	55.0	6.5	88.2
Total Solid, mg/l	1602	750	53.2	2320	774	66.6	2162	7.6	67.3
T.S.S., mg/l	183	39	78.7	201	47	76.6	230	23	90.0
T.D.S., mg/l	1419	633	55.4	2119	697	67.1	1932	625	67.6
Organic, %	806	270	66.5	1057	272	74.3	888	282	68.2

Inorganic, %	796	480	39.7	1263	502	60.2	1275	424	66.7
Lignin, mg/l	97.11	16.0	83.5	505	38	92.5	233	17	92.7
Chloride, mg/l	750	275	63.3	340	175	48.5	562	250	55.5

TABLE – 15

Electrofloculation Studies With Bleach Plant Effluent of a Wood Based Mill

Parameters	**C- stage**			**E- stage**			**`Combined Bleach Effluent**		
	As such	After treatment	% reduction	As such	After treatment	% reduction	As such	After treatment	% reduction
COD, mg/l	490	118	76	1598	125	88	1411	197.5	86
Colour, PCU	305	107	65	3460	346	90	2750	302.5	89
AOX, mg/l	41.4	8.3	80	87.9	13.2	85	50.7	7.6	85
Total Solid, mg/l	3200	1408	56	3460	1211	65	2970	1069	64
T.S.S., mg/l	1789	358	80	40.0	8.0	80	181	38	79
T.D.S., mg/l	1470	588	60	3420	1197	65	2900	1044	64
Organic, %	80.3	24.0	70	42.7	12	72	44.3	15	66
Inorganic, %	19.6	11.8	40	57.3	21.8	62	55.7	20	64
Lignin, mg/l	96.0	19.2	80	595	59.5	90	390	39	90
Chloride, mg/l	759	296	61	766	406	47	1089	512	53

Fig. 13 - Electroflocculation of Bleach Plant Effluent. (Agro Based Mill)

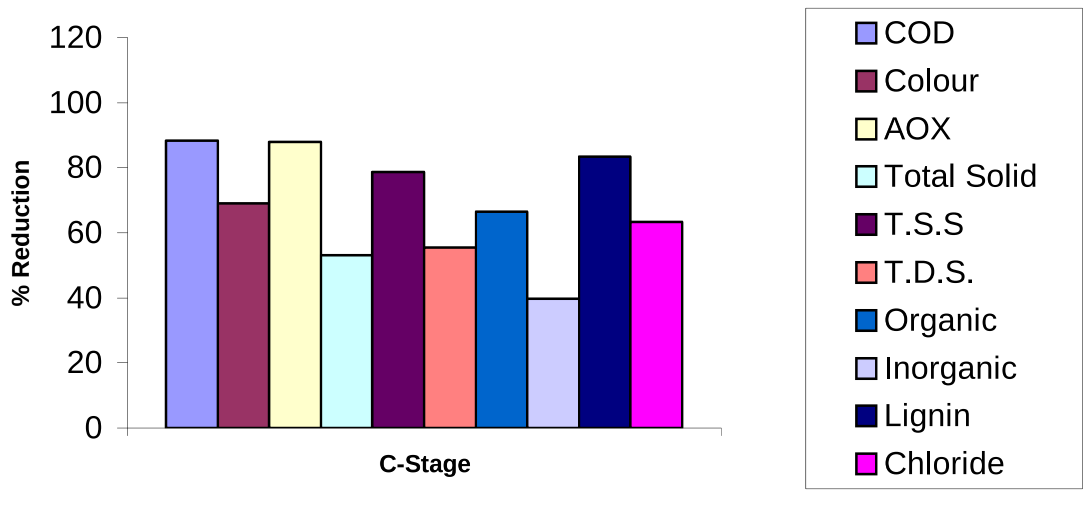
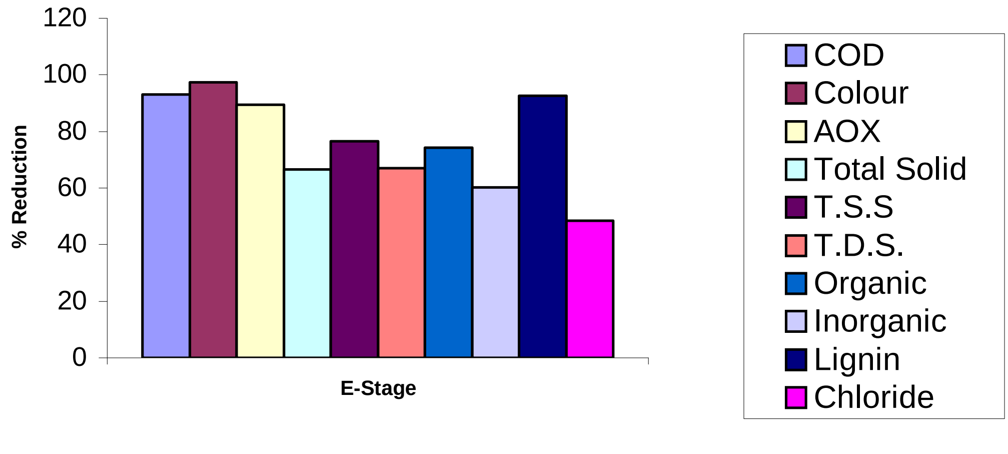


Fig. 14. Electroflocculation of Bleach Plant Effluent. (Agro Based Mill)



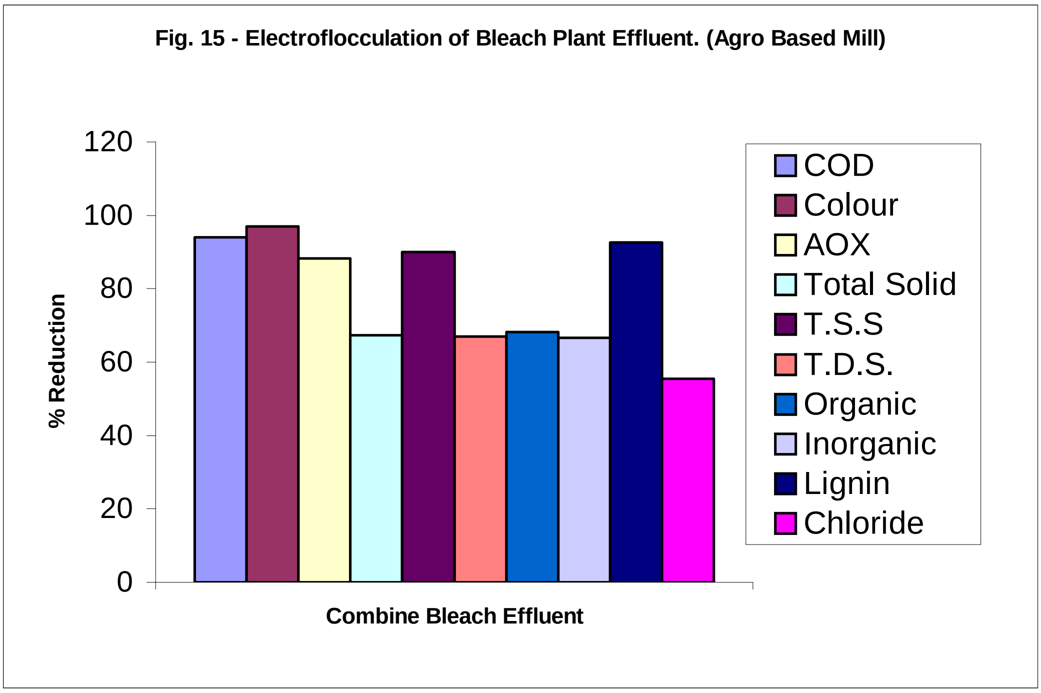


Fig. 15 - Electroflocculation of Bleach Plant Effluent. (Agro Based Mill)
% Reduction
120
100
80
60
40
20
0
Combine Bleach Effluent
COD
Colour
AOX
Total Solid
T.S.S
T.D.S.
Organic
Inorganic
Lignin
Chloride

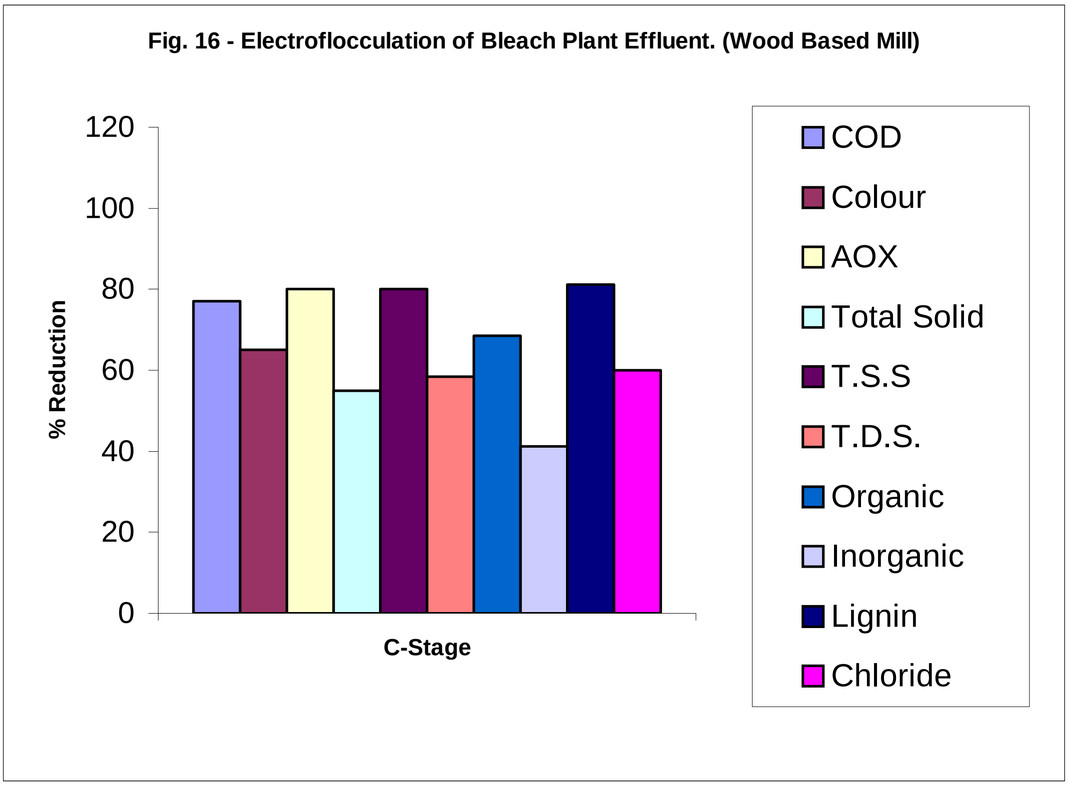


Fig. 16 - Electroflocculation of Bleach Plant Effluent. (Wood Based Mill)
% Reduction
120
100
80
60
40
20
0
C-Stage
COD
Colour
AOX
Total Solid
T.S.S
T.D.S.
Organic
Inorganic
Lignin
Chloride

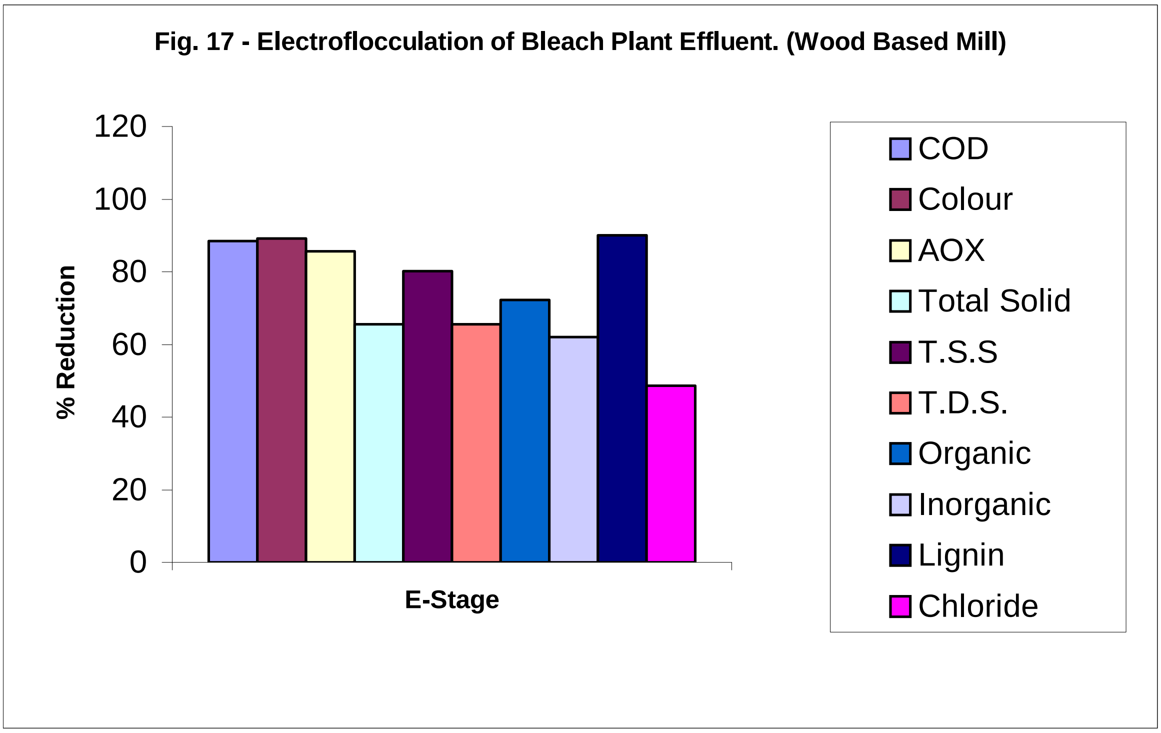


Fig. 17 - Electroflocculation of Bleach Plant Effluent. (Wood Based Mill)
% Reduction
120
100
80
60
40
20
0
E-Stage
COD
Colour
AOX
Total Solid
T.S.S
T.D.S.
Organic
Inorganic
Lignin
Chloride

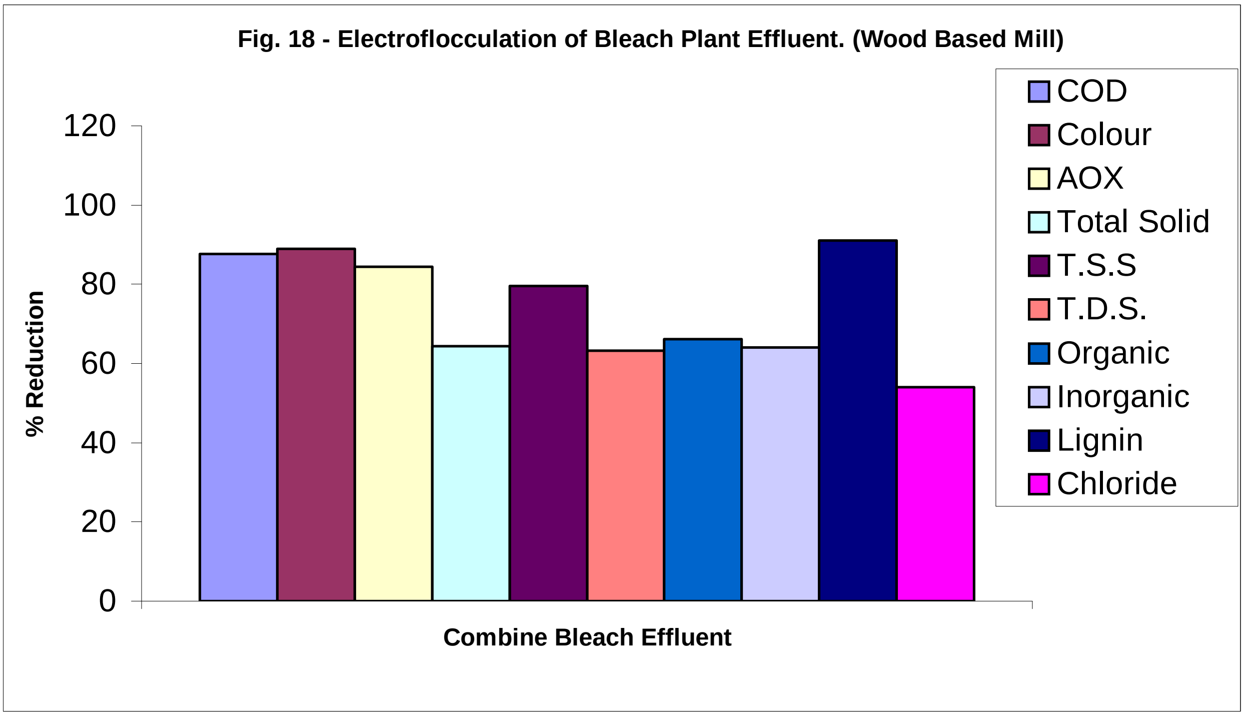


Fig. 18 - Electroflocculation of Bleach Plant Effluent. (Wood Based Mill)
% Reduction
120
100
80
60
40
20
0
Combine Bleach Effluent
COD
Colour
AOX
Total Solid
T.S.S
T.D.S.
Organic
Inorganic
Lignin
Chloride

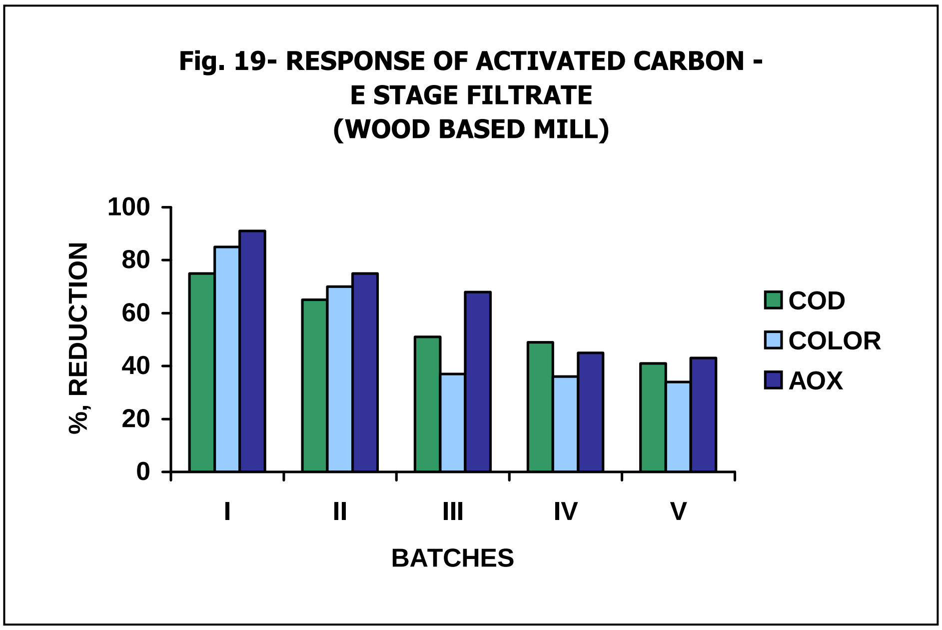
Carbon Adsorption:

In other studies the alkali extraction bleach filtrate (E-stage) collected from wood based mills was 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 colour, COD and AOX. A known amount of bleach effluent was passed through the carbon bed and elutes were collected in batches. The treated sample of each batches was analyzed for COD, colour and AOX reduction. The results obtained are shown in **Table 16 & Fig. 19.** It has been observed that the adsorption efficiency of activated carbon decreased with increased use of carbon bed and the reduction in AOX was decreased from 90% to 40% after fifth batch/cycle.

Table-16

Carbon column – 4.0 inches (E-stage effluent wood based mills)

Parameters	Samples As Such	Ist Filter (Pass)	% Reduction	IInd Filter (Pass)	% Reduction	IIIrd Filter (Pass)	% Reduction	IVth filter (pass)	% reduction	Vth filter (pass)	% reduction
COD mg/l	2163	551	75	749	65	1065	51	1115	49	1269	41
Total solid mg/l	4826	3170	34	3842	20	4032	16	4054	16	4178	13
TDS , mg/l	4173	3088	26	3274	21	3628	13	3498	16	3910	6
Colour (pt. Co. u)	5200	760 colorless + turbid	85	1525	70	3260	37	3350	36	3450	34
Chloride, mg/l	1014	1014	-	1014	-	1014	-	1061	-	1061	-
AOX, mg/l	109	10.0	90.8	-	-	35.3	67.6	-	-	62.5	42.6



Thermal Treatment:

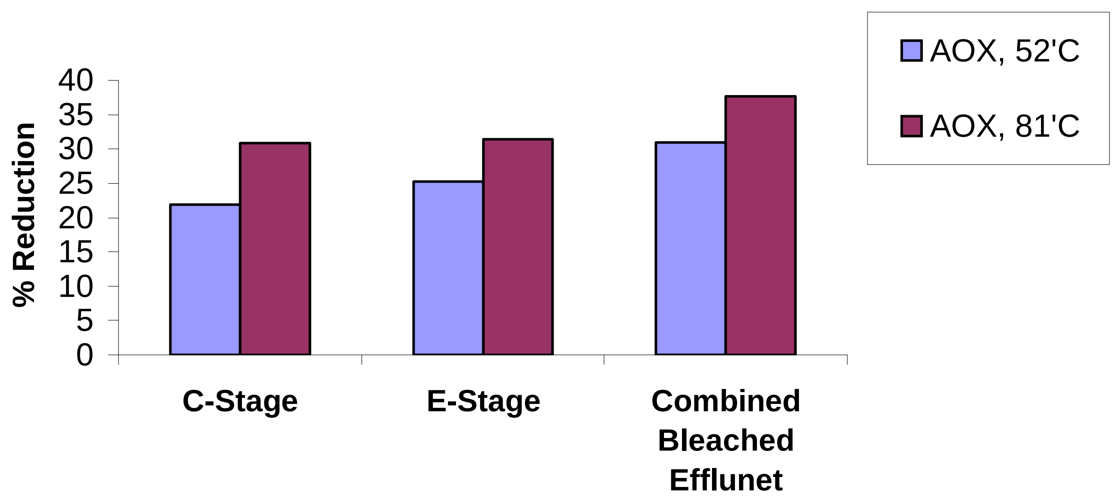
In other studies the effect of heat treatment were also carried out to evaluate the effect of heat treatment on the reduction of AOX on bleach filtrate collected from wood based mills. The results obtained are shown in **Table 17 & Fig. 20**. It has been observed that the reduction in AOX at 50^{o}C and 80^{o}C was 20-25% and 30-37% respectively.

Table-17

Thermal Treatment of bleach plant Effluent (Wood Based mill)

S.No.	Samples	AOX, mg/l As such	Thermal Treatment			
			50^{o}C		80^{o}C	
			AOX, mg/l	% Reduction	AOX, mg/l	% Reduction
1.	C-Stage	46.34	36.20	21.90	32.06	30.82
2.	E-Stage	47.16	35.23	25.30	32.34	31.42
3.	Combined bleach effluent	39.46	30.94	21.60	24.61	37.63

Fig. 20 - Thermal Treatment of Bleach Plant Effluent. (Wood Based Mill)



Toxicity of Bleach Plant Effluent:

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, 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. The toxicity of bleach plant effluents collected from different mills to *Common Corp* (Fish) were tested according to standard method (ISO 6341 1989). The procedure is based upon direct exposure to fish to measure LC_{50} under controlled laboratory condition. The fish of weighing 10-16 gm and length 10-12cm were purchased from a local fish hatchery. Prior to use, the fish were acclimated for two weeks to fresh 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 was stopped 48h before the beginning of each exposure.

Exposures lasting 24h were conducted in glass aquarium of 20 Lit. capacity at a temperature of 25±3^{o}C. Six to eight fish of approximately the same weight and length were placed in aquaria containing effluents. The fish were not fed during experiments but all other parameters were monitored daily.

Toxicity of bleach plant effluents (C-stage, E-stage, H-stage & combined) collected from a wood and agro based mill were determined by using LC_{50} bioassay technique in lab scale aquarium using fish and results obtained are shown in **Fig. – 21 & 22.**

Further the toxicity studies were carried out of the E - stage bleach effluent after chemical treatment with alum and lime. The studies indicate that the mortality rate reduced from 100% (without treatment) to 0% after chemical treatment (i.e. fish survived even after 24 hrs of exposure) **Fig. 23.**

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. The luminescence inhibition tests were accomplished by combining bleach effluents collected from wood and agro based mills with the luminescence bacteria *Vibrio fisheri* NRRL B-11177. The luminescence inhibition (H%) was measured. The results obtained are summarized in **Fig. 24 & 25.**

Toxicity inhibition response of bleach plant effluents on Luminescent bacteria was also evaluated using Microtox Toxicity Analyser which is widely used in developed countries to assess toxicity emission factor and also to establish a correlation between conventional LC_{50} & instrumental Microtox toxicity. Toxicity of combined bleach plant as such, biological treated as such , chemical treated and biological treated (chemical treatment) effluent collected from wood and agro based mills were measured and the results are shown in **Fig. 26 & 27**. The relationship between Toxicity index and AOX is given in **Fig. 28.**

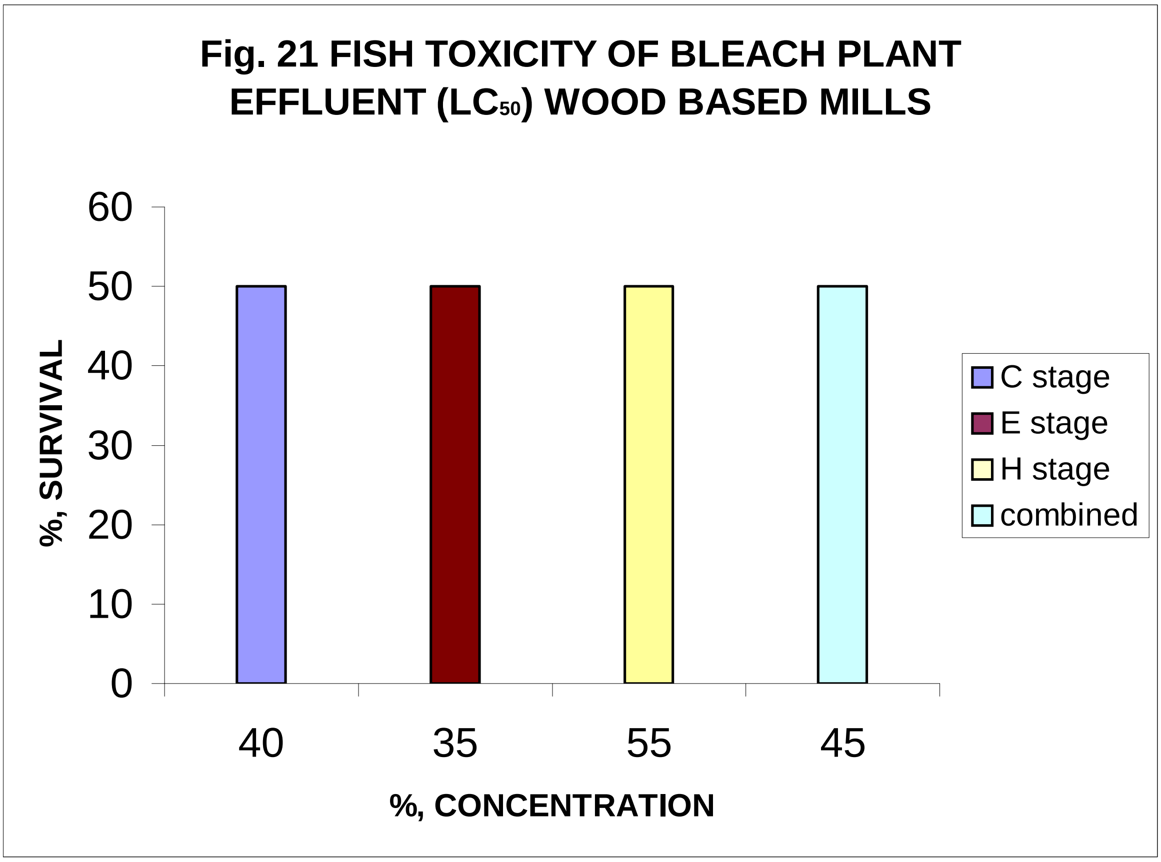


Fig. 21 FISH TOXICITY OF BLEACH PLANT
EFFLUENT (LC50) WOOD BASED MILLS
60
50
40
30
20
10
0
%, SURVIVAL
40
35
55
45
%, CONCENTRATION
C stage
E stage
H stage
combined

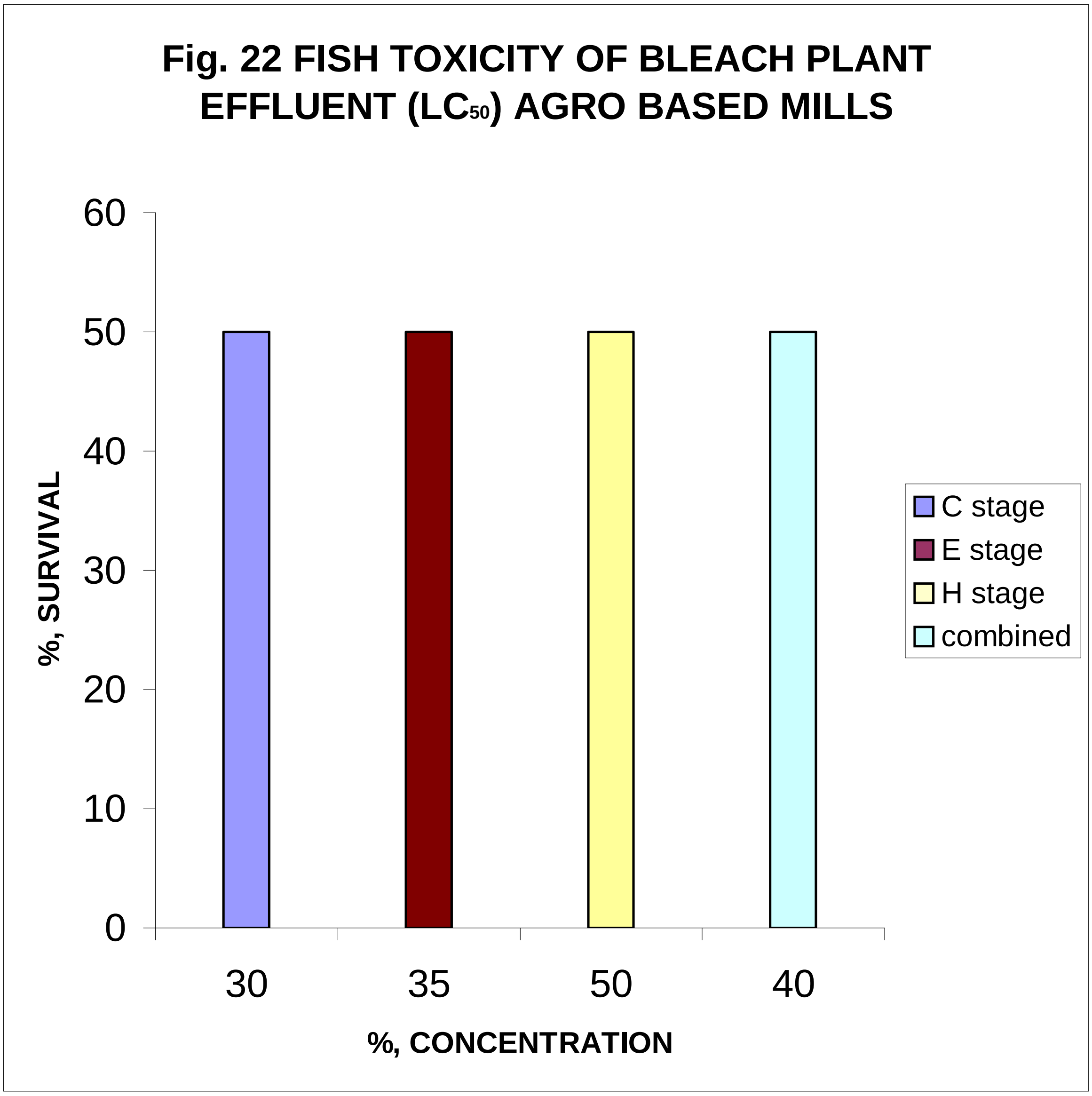
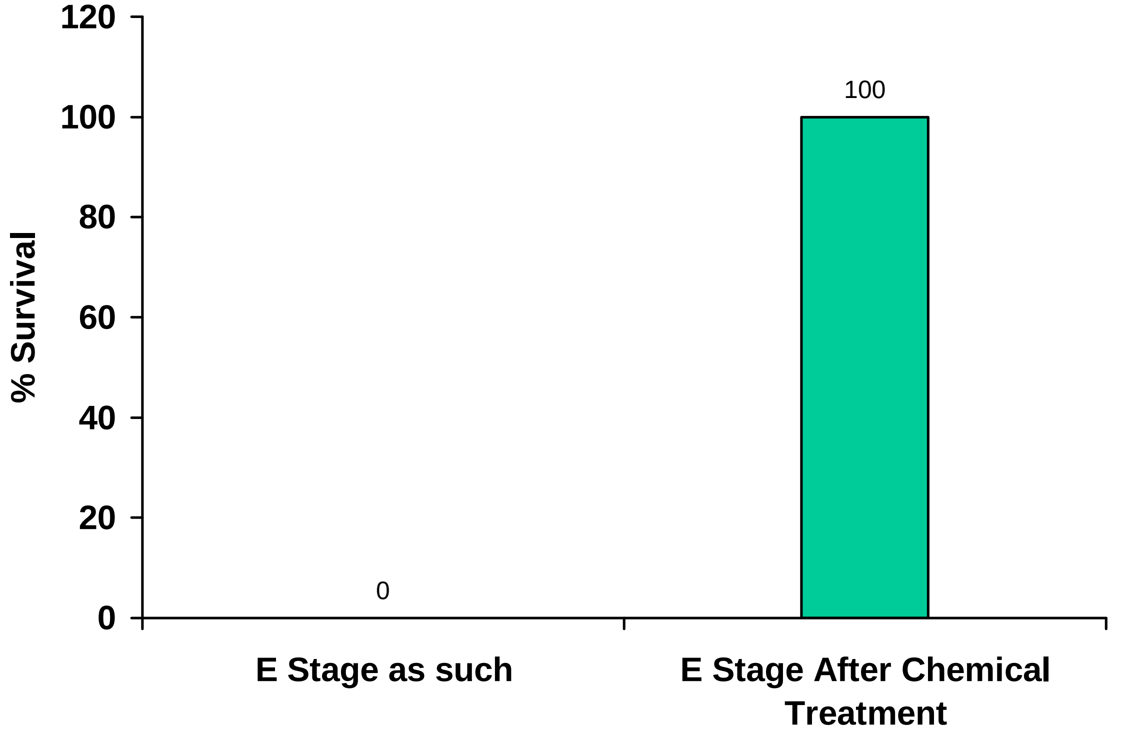


Fig. 22 FISH TOXICITY OF BLEACH PLANT EFFLUENT (LC50) AGRO BASED MILLS
60
50
40
30
20
10
0
%, SURVIVAL
30
35
50
40
%, CONCENTRATION
C stage
E stage
H stage
combined

Fig. 23 Toxicity of Chemicaly Treated effluent (Survival of Fish) one month



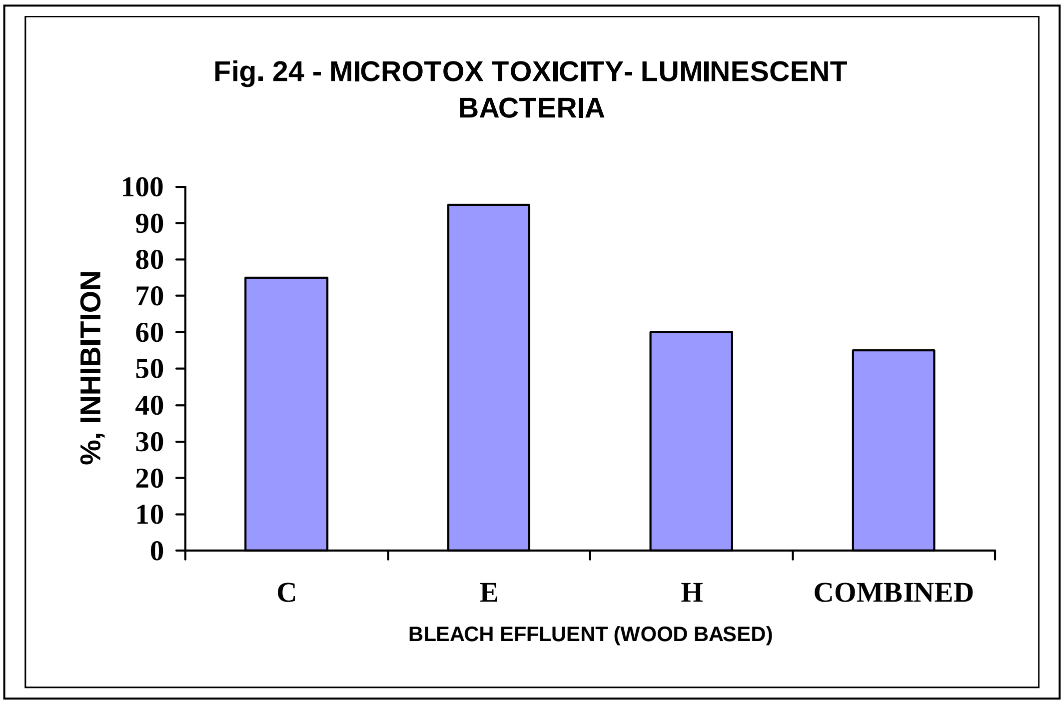


**Fig. 25 - MICROTOX TOXICITY-
LUMINESCENT BACTERIA**

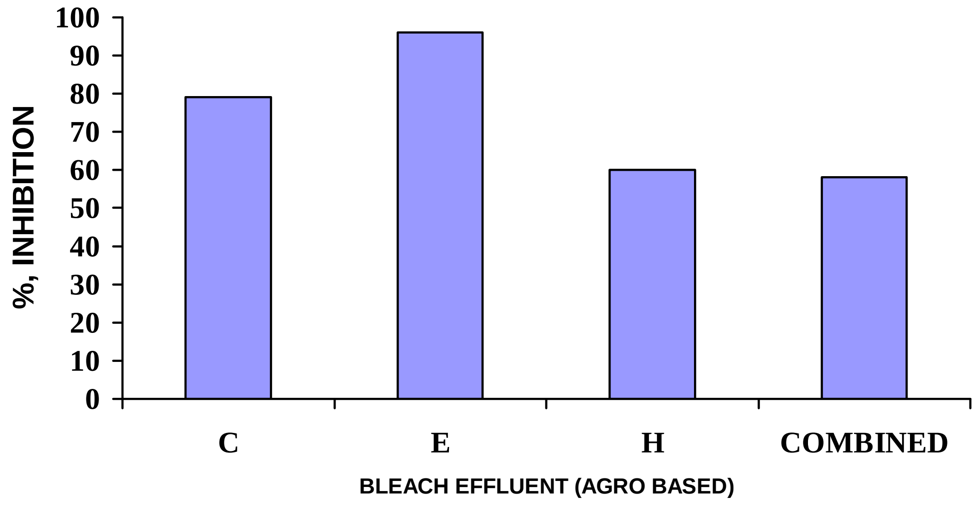
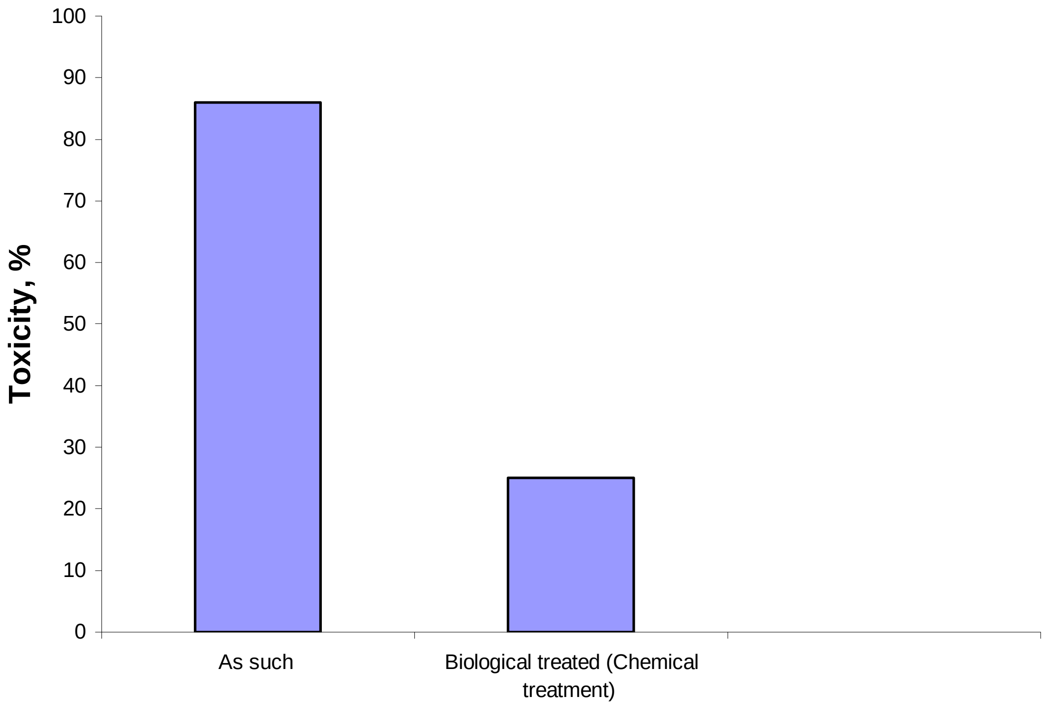


**Fig. 26 Toxicity of Combined bleach plant
(Agro based mill)**



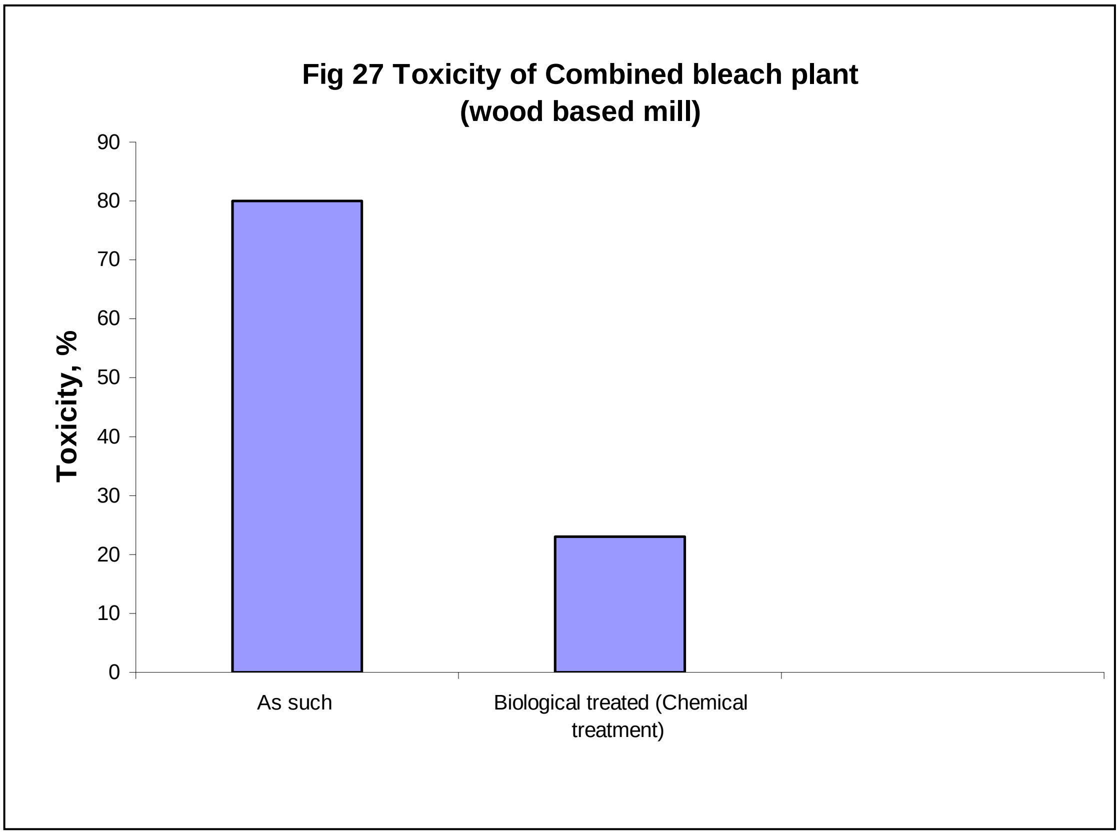


Fig 27 Toxicity of Combined bleach plant
(wood based mill)
Toxicity, %
90
80
70
60
50
40
30
20
10
0
As such
Biological treated (Chemical treatment)

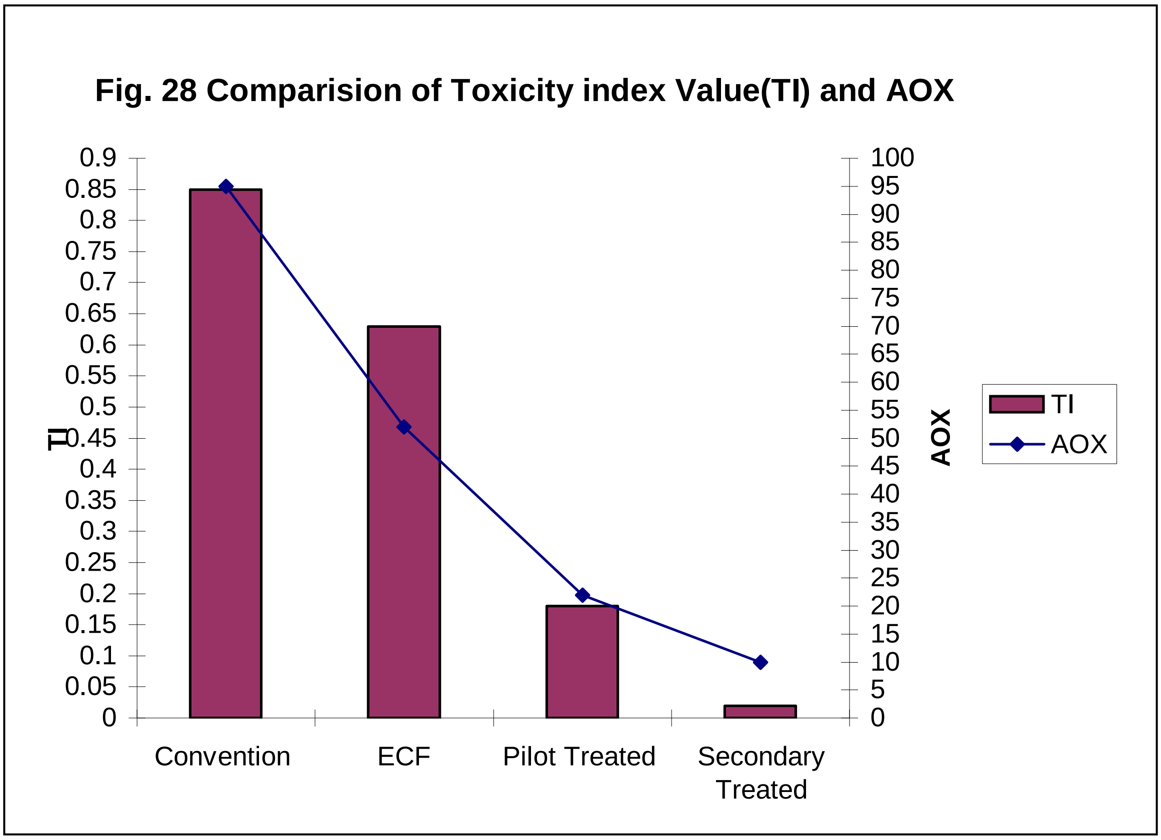


Fig. 28 Comparision of Toxicity index Value(TI) and AOX
TI
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
AOX
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
TI
AOX
Convention
ECF
Pilot Treated
Secondary Treated

Identification of Chlorinated Phenolic Compounds:

All analysis was carried out using HP–6890 gas chromatograph equipped with EC Detector. A HP-1 capillary column was used for all measurements. The column was 30 m in length, with an i.d. of 0.53 mm and a film thickness of 0.25 µ. Injections were made in the split less mode with a 0.8 min purge. The carrier gas used was purified Ar with a column head pressure of 17 psi. The procedures were standardized for identification of chlorophenolic compounds in bleach plant effluents by gas chromatograph. Internal standard 2,3,6 trichlorophenol was used for identification of chlorophenolic compounds. The standard calibration curve for various reference-chlorinated compounds were also prepared in order to identify and quantify of various chlorinated phenolic compounds present in bleached plant effluents. Identification of chlorinated phenolic compounds in bleach plant effluent was carried out by Gas chromatographic techniques. Twelve phenolic compounds have been identified in bleach plant effluents are shown in **Table -18.**

Table -18

	Compounds	**Concentration (µg/l)**
1.	2,4-dichlorophenol	2.3
2.	2,4,6-trichlorophenol	8.5
3.	4,6-dichloroguaicol	2.0
4.	3,4-dichloroguaicol	1.6
5.	4,5-dichloroguaicol	11.5
6.	2,3,4,6-tetrachlophenol	0.8
7.	6-chlorovanillin	16.9
8.	3,4,5-trichloroguaiacol	6.7
9.	4,5,6- trichloroguaiacol	4.7
10.	5,6-dichlorovanillin	13.7
11.	Pentachlorophenol	0.2
12.	Tetrachloroguaiacol	4.2

Biodegradability of Chlorinated Phenolic Compounds:

External effluent treatment like activated sludge process (ASP) is most widely used in pulp and paper industry through out the world. The removal of BOD and acute toxicants (organic chlorine compounds) is largely the result of microbial degradation, physico-chemical process such as adsorption or air stripping. The cellular materials produced during microbial degradation are separated from its suspended liquid by physical process. To study influence of combination of EOP methods, permeate & concentrate obtained from membrane filtration of individual & combined stage bleach plant effluent were subjected to conventional aerobic treatment. The reduction in various pollutional parameters is indicated in **Table 19 & 20.**

TABLE No. –19

Aerobic Biodegradability of Different Fractions of Bleach plant Effluent (Wood Based Mill)

Molecular weight Cut-off	**BLEACH PLANT EFFLUENT**					
	C-Stage		**E-Stage**		**Combined Bleach Effluent**	
	Permeate	Concentrate	Permeate	Concentrate	Permeate	Concentrate
<u>1,000 D</u>						
COD, Red %	62	51	61	53	64	53
AOX, Red %	52	42	50	43	54	43
<u>3,000 D</u>						
COD, Red %	60	55	55	55	56	54
AOX, Red %	46	40	45	38	46	39
<u>10,000 D</u>						
COD, Red %	55	50	57	48	60	54
AOX, Red %	43	35	41	35	43	36
<u>100,000 D</u>						
COD, Red %	50	61	45	59	48	62
AOX, Red %	42	33	40	33	42	35

TABLE No. – 20

Aerobic Biodegradability of Different Fractions of Bleach plant Effluent (Agro Based Mill)

Molecular weight Cut-off	BLEACH PLANT EFFLUENT					
	C-Stage		**E-Stage**		**Combined Bleach Effluent**	
	Permeate	**Concentrate**	**Permeate**	**Concentrate**	**Permeate**	**Concentrate**
1,000 D						
COD, Red %	65	50	60	55	62	55
AOX, Red %	52	40	53	42	53	43
3,000 D						
COD, Red %	58	53	53	50	55	50
AOX, Red %	45	37	44	35	45	37
10,000 D						
COD, Red %	50	45	56	47	57	50
AOX, Red %	50	30	48	34	48	35
100,000 D						
COD, Red %	60	45	58	43	58	45
AOX, Red %	63	28	45	33	50	30

RESULS & DISCUSSION:

Characterization of bleach plant effluent:

- The chemical composition included AOX of bleach plant effluent collected from agro and wood based mill are indicated in (**Table – 12 & 13)**. The results indicated that the AOX generation depends mainly on Kappa number, chlorine dosages and brightness to be achieved, which were also confirmed by results of studies conducted in laboratory using different raw materials (Table **10 & 11).** The level of AOX in bleach effluent of agro based mill is higher compared to that of wood based mill due to use of high dosage of chlorine in agro based mill to achieve desired brightness. Differences in level of other pollutional parameters like COD, BOD, TSS etc. may also be attributed to difference in nature of raw material used, process conditions etc.

Chemical treatment of bleach plant effluent:

- The response of chemical treatment using alum, lime and PAA was evaluated for treatment of bleach plant effluent collected from agro and wood based mills and the results obtained are indicated in **Table 14 & 15**. The results indicate that combination of chemicals was found effective in reduction of pollution load including AOX. A reduction of 50-81%, 50-80% and 83-97% was achieved in AOX, COD and color respectively. The reduction in AOX using chemical treatment depends on nature and molecular size of AOX related compounds. However, in some cases an increased level of TDS in chemical treated effluent was observed due to use of lime.

- The preliminary economics of the lab studies conducted with chemical treatment indicates that the cost of treatment of bleach plant effluent depends on level of AOX, volume of effluent & reduction in AOX to be achieved and it varies approximately Rs. 150-450/t pulp in wood based mill while in case of agro based mill it is around Rs. 250-650/ t pulp.

The analysis of chemically precipitated sludge shows that organic and inorganic content is more or less about 50%

Membrane filtration of bleach plant effluent:

- The bleach plant effluents (C-stage, E-stage, H-stage & combined) were fractionated into various fraction using membranes of different cut-off values like 1,000, 3,000, 10,000, 30,000 and 100,000 D. The aim of the membrane filtration was to evaluate the molar mass of different AOX related fractions, in order make the mass balance of AOX related chloroorganic compounds. The different fractions obtained were analyzed for various pollutional parameters including toxicity and AOX. The mass balance of AOX in bleach plant effluent is indicated in **Fig. 11 & 12**.

- Membrane filtration of bleach plant effluent indicates that around 50-60% of molar mass of chlorinated phenolic compounds are of below 3000D molecular weight, 20-23% are between 10,000D – 1, 00,000D and 14-18% of molar mass is of above 1.00, 000D molecular weight.

Electro flocculation:

- Electrofloculation technique evaluated on lab scale was also found effective in removing of Color, COD and AOX. The reduction in COD, AOX and Color achieved in lab studies was 55-60%, 60-70% and 80-90% respectively **(Table 14 & 15).** However, the technique needs to be demonstrated on mill scale.

Carbon Adsorption:

- Carbon adsorption technique was also evaluated for treatment of bleach plant effluent (E-stage) collected from a wood-based mill. The results (**Table-16 and Fig.- 19)** show that the reduction efficiency of pollutional parameters decreased with increased use of carbon bed.

However, the reduction in COD, AOX and Color obtained were quite encouraging.

- As some of the chlorophenolic compounds are unstable in nature, so the effect of temperature on AOX related compounds was also evaluated and the reduction in AOX achieved varies from 30-37%

Toxicity:

- Bleach plant effluent are major environmental concern as it causes acute and chronic toxicity to the aquatic life. So the toxicity of bleach plant effluents (C-stage, E-stage, H-stage & combined) collected from a wood & agro based mill were determined using LC_{50} bioassay technique in lab scale aquarium using fish. The LC_{50} values obtained are indicated in **Fig. 21 & 22.** The bleach plant effluent has been found toxic to the test fish and 45-50% concentration of bleach plant effluent caused death of 50% test fish under specified condition. Chemical treatment of bleach plant effluent particularly E-stage effluent reduces the toxicity to the level at which no fish toxicity was observed after exposing with chemically treated bleach plant effluent even after one month (**Fig. 23).**

- Toxicity inhibition using Luminescent bacteria a quick test indicator was also evaluated by Microtox Toxicity Analyzer. The results obtained are shown in **Fig. 24 & 25** for wood and agro based mill respectively. Results indicates that E-stage bleach effluent of wood and agro residues are highly toxic and caused 90% inhibition to used luminescent bacteria.

- Laboratory studies on chemical treatment followed by biological treatment of bleach plant effluent were also conducted to assess the biodegradability of AOX. Around 70-75% reduction in toxicity of bleach plant effluent was observed which further improve the biodegradability of AOX compounds. The results obtained are indicated in Fig**. 26 & 27**.

Biodegradability:

- The biodegradability of different fractions of AOX related compound separated using membrane filtration techniques was evaluated in order to assess their behavior in effluent treatment process. The results obtained (**Table 19 & 20**) indicate that the biodegradability of AOX related compounds depends on molecular size of these compounds. The high molecular weight AOX related compounds are resistant and less biodegradable compared to low molecular weight AOX compounds.

Observation & Recommendations:

- The AOX generation depends mainly on Kappa number of unbleached pulp and dosages of chlorine based bleaching chemicals consumption to achieve desired brightness. The level of AOX in Indian Pulp and Paper industry is comparatively high to the mills operating in developed countries even in some Asian countries as most of the Indian mills are continuing with conventional pulping and bleaching technologies.

- The low level of operation of Indian pulp and paper mills is one of the major limitations which restrict them to adopt the modified pulping and bleaching technologies. Due to increased competition from over sea's supply of paper, some of the large scale paper mills have already adopted new eco -friendly technologies and other are in process for the same. However, the high level of AOX in Agro based small scale mills is still a major environmental concern as almost all mills except few are operating without chemical recovery system and produce pulp of high kappa number, which ultimately increases the requirement of bleaching chemicals.

- In view of above mentioned facts and limitation of mills, the end of pipe treatment methods including chemical and physical were evaluated in laboratory. The results indicate the reduction in COD, AOX and colour achieved was 50-65%, 60-80% and 65-85% respectively.

- Based on the project findings, existing technological status as well as limitations of the mills, CPPRI recommends:

    - CPPRI prefer to reduce the discharge of AOX at source rather than end of pipe treatment.

    - Large pulp and paper mills should expand their scale of operation to adopt new environmentally friendly technologies to become competitive and environmentally sustainable.

    - Small scale agro based mills having pulping capacity above 50 t/d, they should expand their pulp mill capacity appropriately to adopt chemical recovery system to produce pulp of kappa number below 18.

    - Mill should improve pulp washing system to minimize carryover of the organic matter along with unbleached pulp entering to the bleach plant.

    - Pulp and Paper mills particularly small mills should use oxidative alkali extraction bleaching to reduce AOX and Color in bleach plant effluent.

    - Mills continuing with conventional process and technology may consider to use the chemical treatment of selected bleach plant effluent streams to reduce toxicity to aquatic life when it is discharged to receiving body.

    - Though the chemical treatment is expansive, the mills particularly agro based mills manufacturing writing and printing paper in absence of chemical recovery system should use physico-chemical methods for treatment of bleach plant effluent to achieve AOX level stipulated by regulatory authorities.

- CPPRI also of opinion that there is need to conduct R & D studies on techno economic viability of membrane filtration techniques as well as management and safe disposal of AOX bearing chemically precipitated sludge.