Toxicity Reduction of Bleach Plant Effluent by using Chemical Additives

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With the introduction of Charter on Corporate Responsibility for Environmental Protection (CREP) the issue reduction / elimination of AOX contributes toxicity has become a top agenda before every pulp & paper mill in India producing bleached variety of paper. As indicated in the charter the large pulp & paper mills have to achieve the AOX level of 1.5 kg/t $_{paper}$ within 2 years and 1.0 kg/t $_{paper}$ within next 5 years. Small mills will have to either install chemical recovery system or shift to waste paper to continue their operations. The reduction in AOX to the target level given in CREP involves the adoption of new fibre line including modern technologies. With high capital investment involved in the switching over to new fibre line, the mills are urgently looking forward to suitable alternate treatment options to reduce the AOX level. In this perspective studies being conducted by CPPRI on the effectiveness & feasibility of use of chemical additives as well as other physical treatment techniques like electroflocculation, membrane filtration, adsorption etc. for reducing the toxic AOX related compounds in bleach plant effluents assumes significance. The present paper discuss the results of these studies which can help the mills in reducing their AOX level to a significant extent.

INTRODUCTION

In international perspective, the issue of AOX is not new. However in Indian context the awareness and the concern about AOX and its control has grown in last few years only. While by switching over to new fibre line (involving modern technologies in pulping, bleaching, pulp washing etc), the mills in developed countries have reduced the AOX below toxicity level and it is now no longer a major issue, the mills in India producing bleached variety of paper have continued to use elemental chlorine for bleaching (in most cases) due to techno- economical reasons. With growing public awareness, preference for eco friendly products in national & international market and stricter environmental legislations, the mills have been forced to develop / adopt suitable strategies to reduce the AOX level. Further **"Charter on Corporate Responsibility for Environmental Protection (CREP)"** introduced by CPCB recently has increased the pressure as well as forced the mills to reduce the AOX level in a fixed time frame as mentioned in Table 1. Achieving the AOX discharge standards as specified in CREP is a great challenge as the level of AOX discharged in Indian paper industry generally varies between 1.0 -2.5 kg/t$_{paper}$ in large mills and 4.0- 6.0 kg/t$_{paper}$ in small agro based mills.

Formation of Chlorinated Phenolic 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 Fig -1 which include chlorinated resin acids, fatty acids, chlorinated phenolics, dioxins & furans. The amount of chlorinated organic compounds produced during pulp bleaching varies with raw materials, kappa number of the pulp, bleaching sequences & conditions employed.

Fig-2 illustrates that 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. 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.

Environmental Impact of Chlorinated Organic Compounds

The chlorinated organics compounds formed during bleaching of pulp with chlorine and chlorine based chemicals are partly responsible for contributing effluent colour, acute / chronic toxicity, mutagenicity

Table -1 AOX Discharge Standards as per CREP

Mill category	Environmental issues	Implementation Schedule
Large Paper Mills	Discharge of AOX kg/t_{paper}	AOX 1.5 kg/ t_{paper} within 2 years AOX 1.0 kg/ t_{paper} in 5 years
Small Paper Mills	Compliance of standard of BOD, COD & AOX	Either achieve the discharge Standards 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
	Upgardation of ETPs so as to meet discharge standards	Upgrade the ETP within one year so as to achieve the discharge standards

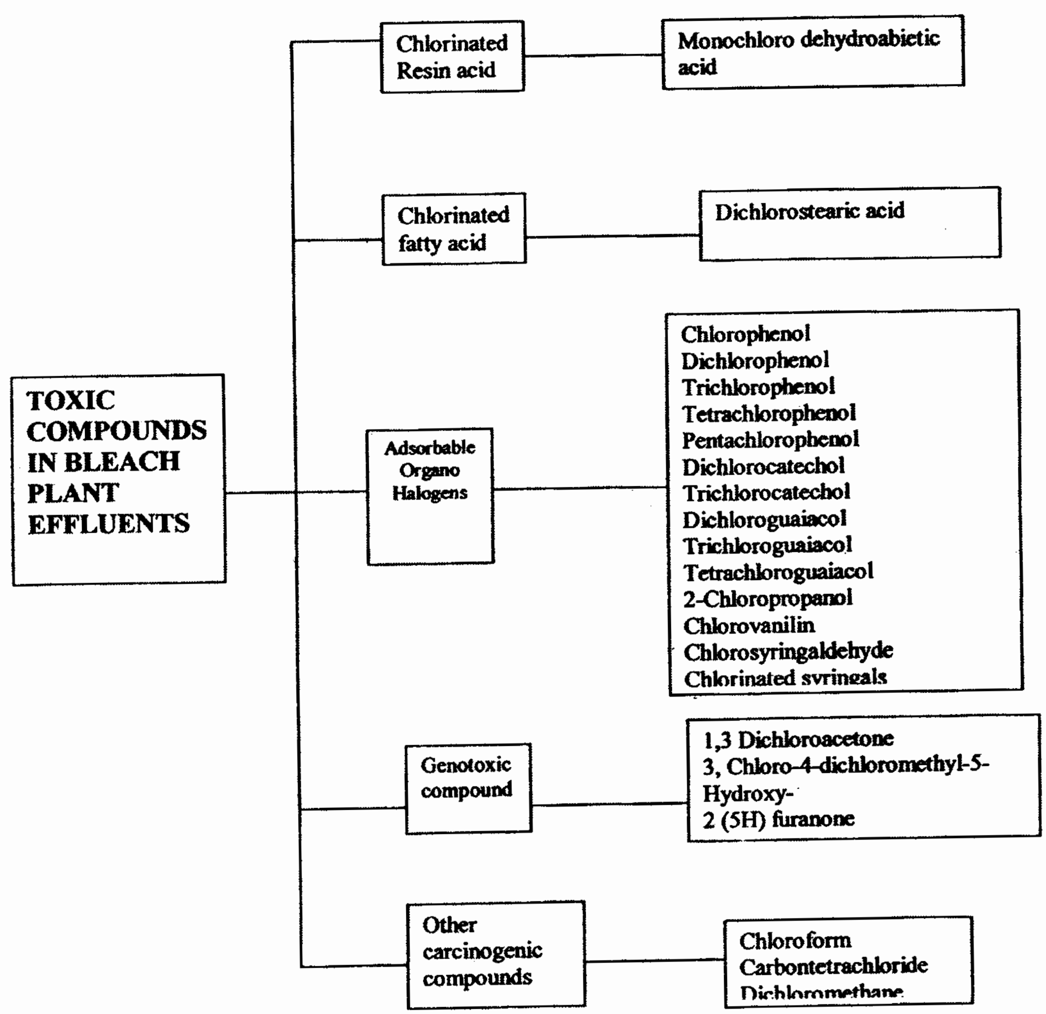

Fig.1 Toxic Compounds in Bleach Plant Effluents

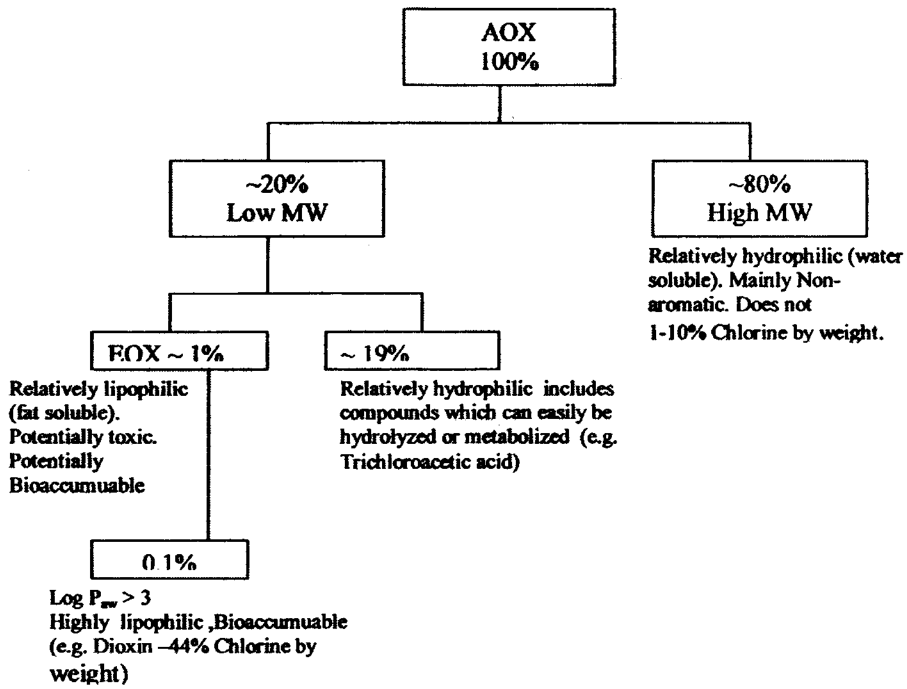

Fig.2 Distribution of Chloro Phenolic Compounds

and carcinogenicity. The toxicity of chlorinated compounds increase with an increase in the number of chlorine atoms in an organic compounds. The chlorinated organic compounds present in alkali extraction stage (E) bleach effluent are found more toxic and contributes more than 90% of acute toxicity. The major species of the chlorocompounds like trichlorophenol, tri & tetra chloroguaiacols have tendency to accumulate in fish & are responsible for acute toxicity. The formation of these compounds are directly proportional to the consumption of chlorine. Chloroform and carbon tetra chloride produced during bleaching of pulp have also .been classified as carcinogenic. The hypochlorite bleaching is the major contributor of chloroform & is reported as high as 0.30 kg/t_{pulp}. The various chlorinated benzene, phenols, epoxystearic acid and dichloromethane present in bleach effluent have also been classified as suspected carcinogens.

Polychlorinated Dioxins And Furans

Among the chlorinated phenolic compounds, the dioxins and dibenzofurnas are a group of chlorophenolics which have been found to have toxic effects. The prominent among the dioxins are 2,3,7,8 tetra chloro dibenzodioxin (TCDD) and 2,3,7,8 tetra chloro dibenzofuran (TCDF). It is estimated that out of 100% AOX the percentage of dioxins is less than 0.1 % which is supposed to be highly lypophyllic and bioaccumulable compounds. Such compounds are formed when unchlorinated dibenzodioxin (DBD) and dibenzofuran (DBF) present in unbleached pulp are chlorinated in chlorination stage. The oil based pulp mill additives particularly brown stock defoamer 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}. It has been observed that major source of chlorinated dioxins is the C-stage effluent and the formation of dioxins is mainly dependent upon:

- Brown stock kappa number
- Active chlorine multiple
- Mixing conditions during chlorination
- Carryover of COD and
- Wash water quality

Fish exposed to chlorinated phenolics discharge by bleached pulp mill 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. Some of the biological affects observed in laboratories and field studies are summarized below:

- **Acute toxicity:**
- Egg mortality
- Percentage of fertilised egg.
- Acute toxicity to newly hatched fry.
- **Late effects: Survival and stress tolerance of fry from exposed parents.**
- **Effects on behavior: Response to rotory flow**

Table -2 Risk Dose & Toxic Effects of Dioxin

Agency/Country	Risk dose	Toxic/health effect
EPA	6.4 x10^{-3}*	Cancer
Germany	1.0*	Cancer/reproductive
Netherland	4.0*	Cancer
Switzerland	a**	
FDA	5.7x 10^{-2}	Cancer

- **Physiological and Histological sublethal effect:**
- Growth rate
- Histological changes in lever.
- Occurrence of parasitic in gills of flounder
- **Bioaccumulation:**
- Effect on primary production in natural mixed phytoplankton populations.
- **Genotoxic effects:**
- Mutagenic effects
- Carcinogenic effects.

Dioxin have received extensive media attention and it is reported that 2,3,7,8 Tetra chlorodibenzo dioxins is extremely toxic and bioaccumulative. Dioxins even in trace amounts are reported to cause a wide range of other adverse effects on human health condition including

- Disruption of regulatory hormones.
- Reproductive and immune system disorders and
- Abnormal fetal development.

The toxic effect and toxic levels of dioxins fixed by different countries and agencies are indicated in Table -3.

Technological Developments to Reduce AOX

In developed countries adoption of Extended & oxygen delignification process & substitution of elemental chlorine based bleaching with ECF & TCF bleaching sequence are the major technological developments aimed at reducing / eliminating the discharge of AOX. The other measures tried / adopted successfully have been - Improved pulp washing techniques to minimize the carry over of organic matter alongwith unbleached pulp,. Elimination of use of oil based defoamers in pulp washing, Use of oxidative alkali extraction bleaching, Elimination of hypochlorite bleaching etc.

Table -3 Characterization of bleached plant effluent collected from wood based mill

Parameters	C-stage	E-stage	H -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
Colour, PCU	305	3460	424	2750
Organic, %	46.0	42.7	42.7	44.3
Inorganic, %	54.0	57.3	57.3	55.7
Lignin, mg/l	96	595	158	390
AOX, mg/l	41.4	87.9	70.5	50.7

Table -4 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/I	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, %	50.3	45.5	47.8	41.0
Inorganic, %	49.7	54.5	52.2	59.0

However the application of new pulping and bleaching technologies have been limited in Indian context so far mainly because of:

- Requirement of high capital investment
- Low scale of operation
- Use of mixed raw materials
- Feasibility & economic viability not encouraging (in most cases)

In such scenario physico -chemical treatment options offer a possibility for reduction in AOX level. Exhaustive studies are being carried out at CPPRI in this area with an objective to evaluate techno - economic feasibility of these end of pipe treatment (EOP) methods for treatment of bleach plant effluent in order to reduce the pollution load and its toxicity as well as help the mills to meet the discharge standards related to AOX .

Experimental Studies

At the outset . bleach plant effluents were collected from an agro based and a wood based mill using chlorine based conventional bleaching sequences. The effluent from individual stage as well as combined were characterised to assess the level of various pollutional parameters. The results of analysis are indicated in Table 3 & 4. Based on the results necessary work plan was formulated for treatment of the bleach plant effluent.

Treatment of Bleach Plant Effluent

The treatment options involved two way approach i.e. :

- Chemical treatment methods Precipitation. Coagulation.etc.) and
- Physical treatment methods

(Electrofloculation. Membrane filtration and Adsorption techniques)

Chemical Treatment Studies

The studies were focused mainly to optimize the dosages. treatment conditions. combination of chemical additives to reduce the level of toxic material in bleach plant effluent. Various trials with chemical additives generally used by industry like lime alum. PAA were undertaken individually & in combination to evaluate their response in reducing the level of chlorinated phenolic compounds. The dosage of chemical additives were optimized on the basis of reduction in pollutional parameters after a number of trials. The basis for addition of chemical additives was taken as COD of the efftluent. The response of various chemical additives used for treatment of bleach plant efftluent are tabulated in Table - 5 & 6.

Physical Treatment Methods

The physical treatment methods involved the use of membrane filtration, electrofloculation and adsorption techniques for treatment of bleach plant effluent.

Electrofloculation

Electrofloculation studies were carried out in a lab fabricated electrolytic cell. The alkaline extraction stage bleach effluent was treated using Electrofloculation technique. The results obtained are indicated in Table -7.

Membrane Filtration

The aim of the membrane filtration was to determine the higher & lower molecular wt fractions present in bleach plant effluent & make the mass balance. Accordingly ,the bleach plant effluents (C-stage, E-stage, H-stage &

Table-5 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 : I	0.5 : 1	1.5 : 1
P AA, 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

combined) were fractionated into various fraction through membrane filtration using different cut-off values of membranes like 1,000 , 3,000 , 10,000 , 30,000 and 100,000 D. The permeate and concentrate obtained were analysed for various pollutional parameters including toxicity and AOX. The mass balance of AOX in bleach plant effluent of agro & wood based mills is indicated in Fig. 3 - 4 .

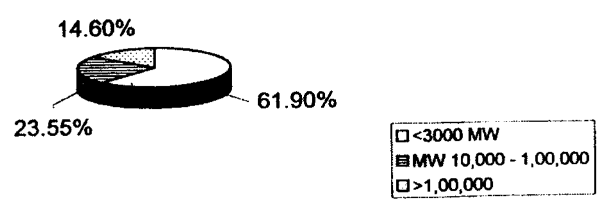

Fig .4 AOX Fractions - Bleach Plant Effluent (Wood Based Mill)

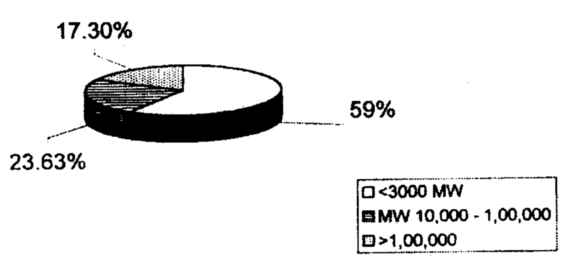

Fig .3 AOX Fractions - Bleach Plant Effluent (Agro Based Mill)

Carbon Adsorption

The carbon adsorption technique was evaluated for treatment of the alkali extraction bleach filtrate (E-stage) collected from a wood based mill. 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 a column of carbon bed and elute were collected in batches. The treated sample of each batch was analyzed for COD, colour and AOX reduction. The results obtained are shown in Fig. 5

Toxicity of Bleach Plant Effluent (Fish Toxicity)

Toxicity of bleach plant effluents (C-stage, E-stage, H-stage & combined) collected from a wood based mill were determined by using LC_{50} bioassay technique in

Table -6 Chemical treatment of bleached 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/I	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			
pH	5.5	5.5	5.5
COD mg/I	240	596	306
AOX mg/I	18.14	25.43	13.23
colour, PCU	67.0	363	61.0
(D) Removal Efficiency, %			
COD	72	80	50
AOX	61	81	65
Colour	83	97	94

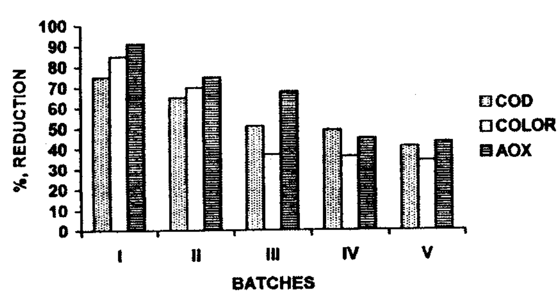

Fig .5 Response of Activated Carbon - E Stage Filtrate (Wood Based Mill)

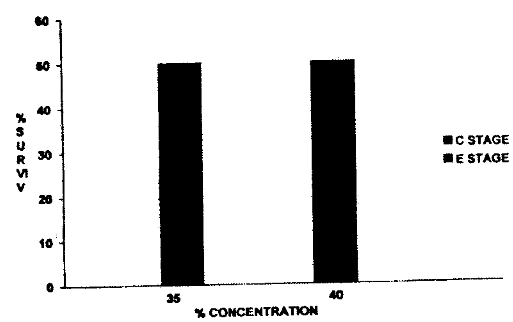

Fig .6 Fish Toxicity of Bleach Plant Effluent (LC_{50})

lab scale aquarium using fish. The results are indicated in Fig. 6. Further the toxicity studies were carried out of the E - stage bleach effluent after chemical treatment with alum and lime.

RESULTS & DISCUSSIONS

The above studies indicate that treatment of bleach plant effluent by use of chemical additives have a good potential in reducing the AOX level as well as other pollutional parameters. Combination of chemicals like alum, lime and PAA have been found effective in reduction of pollution load to an encouraging level of 50-80%, 50-80% and 80-95% in terms of reduction in COD, AOX & colour respectively. The use of chemical additives is also beneficial in reducing the toxicity of bleach plant effluent.

No fish toxicity was observed after chemical treatment of bleach plant effluent. 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)

The preliminary economics of the use of chemical additives (based on mill figures) 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

Table - 7 Treatment of bleach plant effluent through electrofloculation (wood based mills)

Particulars	Untreated Eop effluent	Treated Eop effluent 2 Lit. volume	% Reduction	Treated Eop effluent 5 Lit. volume	% Reduction
pH	11.7	9.3	-	8.5	-
COD, mg/l	1159	395	66	458	61
BOD, mg/l	178	69	61	105	41
AOX, mg/l	42.8	10.5	76	14	67
Colour, PCU	1133	60	95	135	88
Power consumption Watt h. / l	-	21	-	11.6	-

150-350/ t_{pulp} & Rs 400- 650 / t_{pulp} respectively.

However, inspite of its effectiveness in reducing the pollution load. the use of chemical additives is associated with some bottlenecks, limitations which needs to be addressed.

such as

- Increased level of TDS in treated effluent
- Disposal of precipitated sludge

The results obtained in laboratory studies on Electro flocculation have been found encouraging and the reduction in COD.AOX & Colour achieved was 60%. 67% & 88% respectively. The main advantage of Electrofloculation technique is easy and effective separation of lignin at very lower input of electric current. The analysis of chemically precipitated sludge indicates presence of around 90% organics which gives possibility for incineration in a boiler or lime kiln. However, the technique needs to be demonstrated on mill scale.

The mass balance studies conducted to identify the distribution of molecular weight of phenolic compounds indicates that more than 60% of molar mass of chlorinated phenolics are below 3000 D which are easily degradable in biological treatment system while remaining 40% molar mass is having molecular weight which are usually non biodegradable.

The study on effect of adsorption by activated carbon indicate that though the treatment is effective in reducing the pollution load. The adsorption efficiency of activated carbon decreases with increased use of carbon bed as the reduction in AOX decreased from 90% to 40% after fifth batch/cycle.

CONCLUSIONS

The discharge of AOX in Indian mills is comparatively very high as most of these mills use high dosages of chlorine based bleaching chemicals for bleaching of high kappa number pulp to achieve the desired brightness. The CREP charter introduced recently calls for appropriate measure within a fixed time frame to meet the discharge standards. Low scale of operation & high capital investment are the major constrains for immediate switching over to new fibre line for reducing the AOX. Moreover the suitability of these modern fibre line for mixed raw materials is also debatable. So a twin way approach involving both inhouse control measures and EOP treatment options is the best possible way at present to comply with the proposed environmental discharge norms. Though the chemical precipitation has some limitations, however, the studies being conducted on use of chemical additives & physical techniques for treatment of bleach plant effluents by CPPRI holds significance and importance specially for Indian mills having low scale of operation using agro residues as well as wood based raw materials.

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