

ADSORBABLE ORGANIC HALIDE (AOX) LEVEL AND THEIR REDUCTION BY CHEMICAL TREATMENT OF BLEACH PLANT EFFLUENT OF AGRO AND WOOD BASED PULP AND PAPER MILLS

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ABSTRACT

During bleaching of pulp for making paper, a lot of effluents are generated which contain different type of chloro organic compounds collectively known as Adsorbable Organic Halide (AOX). AOX is known as toxic chemical and it must be treated before release in the water stream. Bleach plant effluent from Agro based pulp and paper mills releases high amount of AOX compounds as compared to the wood based mills. Results shows that Extraction -stage bleach effluent are significant of AOX compounds as compared to other stage effluent. The adoption of new technologies like extended and oxygen delignification, ECF & TCF bleaching involves huge capital investment as most of these process and equipments are of imported origin. The treatment of segregated bleach plant effluents with combination of chemical (Lime, Alum & Polymer) is the suitable to reduce the AOX by about 50-60% and ultimately reduces the toxicity of effluent.

INTRODUCTION

Pulp and Paper Industry is one of oldest industries. A rapid development and introduction to mill scale of new & modified techniques for production of bleached kraft pulp has occurred in developed countries and this development is for reduction of lignin entering to bleach plant. Effluents originated in cellulose pulp manufacturing processes are usually toxic and recalcitrant, specially the bleaching effluents, which exhibit high contents of aromatic compounds (Chaparro, *et al.*, 2010). Indian pulp and paper mills however continue to use conventional pulping and bleaching technologies primarily because of low

scale of operation, use of mixed fibrous raw materials and high capital investment. Most of the mills producing bleached variety of paper use high dosage of chlorine to bleach the pulp to high brightness of papers which results into generation of high level of chloro organic compounds collectively known as Adsorbable Organic Halide (AOX) (Suntio, *et al.* 1988). Identification & quantification of individual chloroorganic compounds is exceedingly complex and so generic measurement is desirable whereby the total amount of chlorine bound to organic matter is quantitatively determined (Odendahl *et al.* 1990). A simple and economical method for estimating the

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amount of chlorinated organic material is AOX (Earl and Reeve, 1989). 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 *et al.* 2001). The hazardous effect of bleach plant effluent was considered related to use of elemental chlorine for bleaching of pulp. 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, 1991). In early 70's the major portion of lignin was usually removed in subsequent bleaching stage of pulp produced with high kappa no. as the conventional pulping process was having limitation to produce pulp of kappa no. below 20 and secondly, because environmental issues were not given the priority due to non availability of analytical method for testing of effluents for AOX (CPPRI Reports). 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, *et al.* 1996). The increased environmental consciousness of the public particularly in developed countries has made AOX a major environmental issue when the found chloro organic compounds in fish fat stocks receiving bleach plant effluent. Murray and 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. The detection of toxic chloro organic compounds, imposition of stringent norms has necessitated the pulp and paper industry to identify the areas and development of technologies to reduce the discharge of chlorinated compounds. We should care about AOX in our environment because many organochlorines have been shown to have toxic effects. Several pulp and paper mills across Canada have been legally charged for failing their effluent toxicity limits, and this trend is likely to continue if regulators feel public pressure to enforce environmental regulations (Riebel, 1997). There are many options to reduce the AOX value with advantage and disadvantage with regard to capital costs, operating costs, ease of retrofit, fabrication and installation time. A number of factors are to be considered before selection of any

treatment system (Bajpai and Bajpai, 1997). Chemical precipitation of chlorinated organic material by iron and or aluminum salts has been reported as a potential AOX removal system (Wilson and Holloran, 1992). Adsorbable organic halides (AOX) can be efficiently reduced by adsorption, ozonation and membrane filtration techniques (Pokhrel and Viraraghavan, 2004). In small agro based pulp mills, the scenario of AOX discharge is more alarming as compared to large wood based mills as small mills are using high dosages of chlorine to bleach pulp of high kappa number due to economical reasons. The present paper highlights the chemical treatment of bleach plant effluent with evaluation of chemicals and optimization of treatment condition and dosage.

MATERIALS AND METHODS

Bleach plant effluents were collected from the agro based mills and wood based mills. The effluent of chlorination stage, extraction stage and combined stage were initially characterized for generation of AOX and then treated chemically to achieve reduction in AOX compounds. Hypo stage effluents in most of the mills are utilized in the process itself.

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

- For each chemical treatment, 100 mL of sample were taken in the beaker. The alum and lime (procured from the mill) were added and stirred for few minutes. The doses of chemical for the treatment were fixed on the basis of COD.
 - The doses of chemicals were optimized for improved reduction of AOX.
 - Polymer was used for the better settleability 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 mills and wood based mills are shown in Fig. 2 & 3.

RESULTS

The results show that the Extraction stage effluent was having high AOX value (agro- 95-109 mg/L

and wood 88 - 98 mg/L) as compared to other stage bleach effluents as shown in Fig.1. On the basis of characterization of both agro and wood based bleach effluent, bleach plant from agro based small mills was giving more AOX value than the bleach plant of wood based large mills (Fig.1) due to use of high chlorine consumption during bleaching of pulp for economic reasons. The AOX value in bleach plant effluent is given in the Fig. 1. The response of simultaneous coagulation / precipitation by using

alum, lime and Polymer has been evaluated for treatment of bleach plant effluent collected from agro and wood based mills. The dose of lime and alum were optimized and treated the three samples for their repeatability. All the results obtained indicate their reduction in Fig. 2 & 3 for agro and wood based mill. 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. Percent reduction of

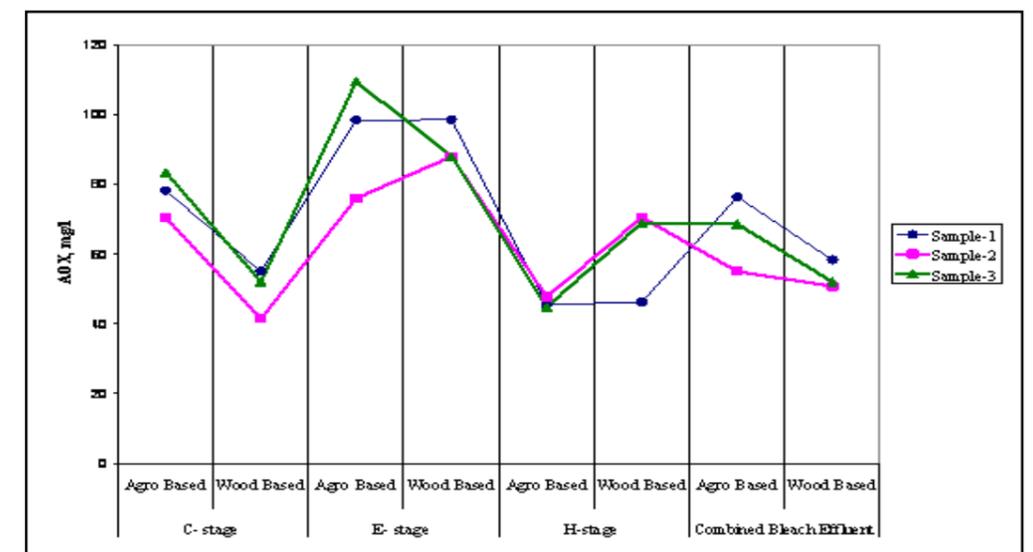


Fig. 1 AOX value in Agro based Mills & Wood Based Mills

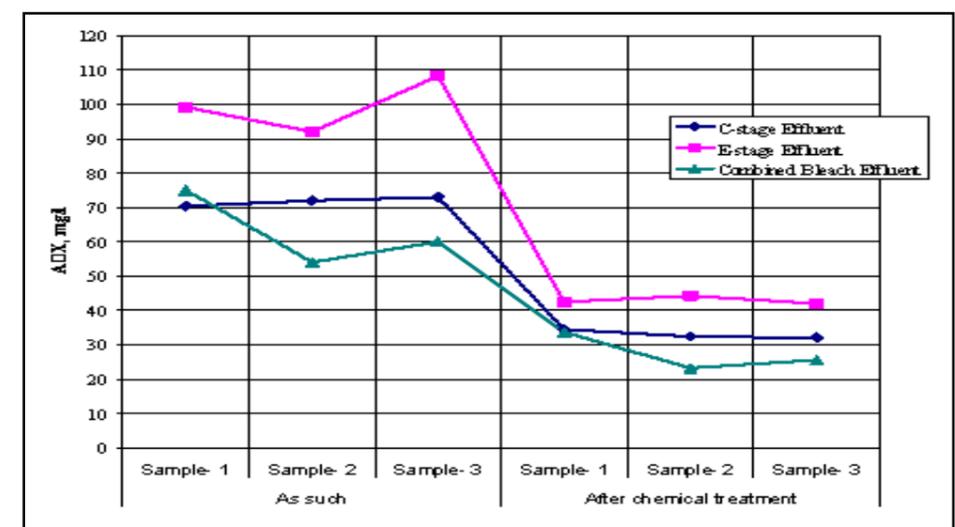


Fig. 2 AOX reduction by chemical treatment (Agro based Mills)

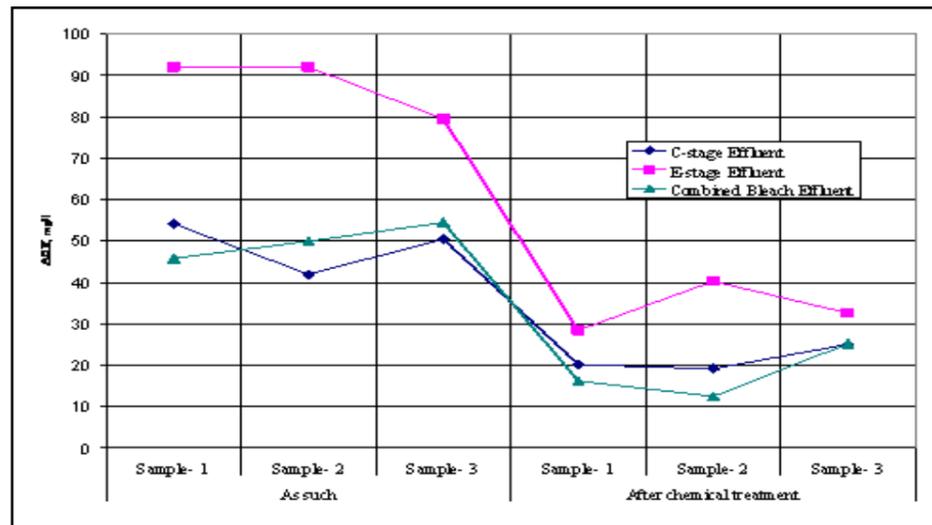


Fig. 3 AOX reduction by chemical treatment (Wood based Mills)

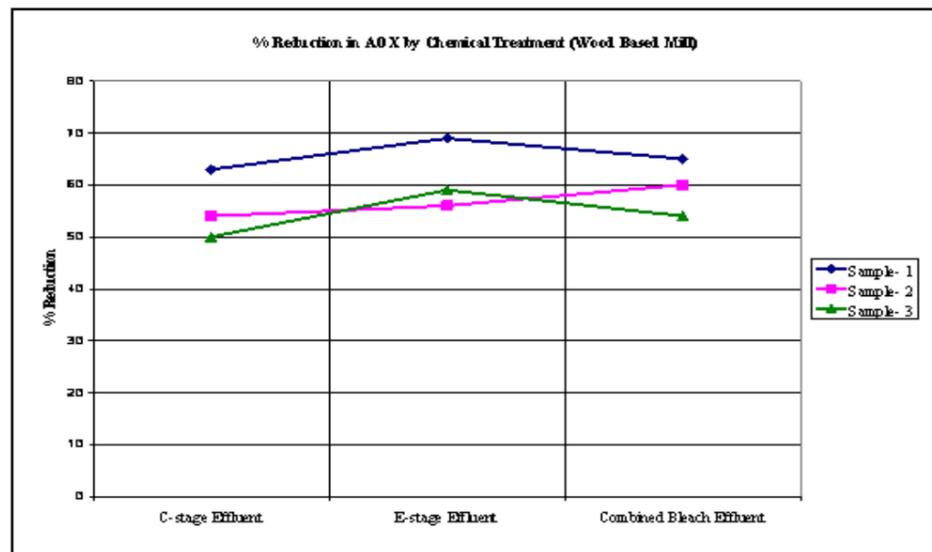


Fig. 4 Reduction % in AOX by Chemical treatment (Wood based mill)

AOX in different stages of Bleach plant effluents of Agro and wood based mills are given in Figs. 4 & 5.

Around 51- 56% AOX reduction was achieved in C- stage, 52-61 % in E- stage and 55-58% in combined bleach plant effluent of agro based mill. Around 50-63% AOX reduction was achieved in C- stage, 56-69 % in E- stage & 54-65% in combined bleach plant effluent of wood based mill. Earl and Reeve, 1989 has been reported that AOX reductions of only up to 30% can be achieved by neutralization of kraft mill bleach

plant effluent to pH 7 with caustic soda. Milosevich, and Hill, (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

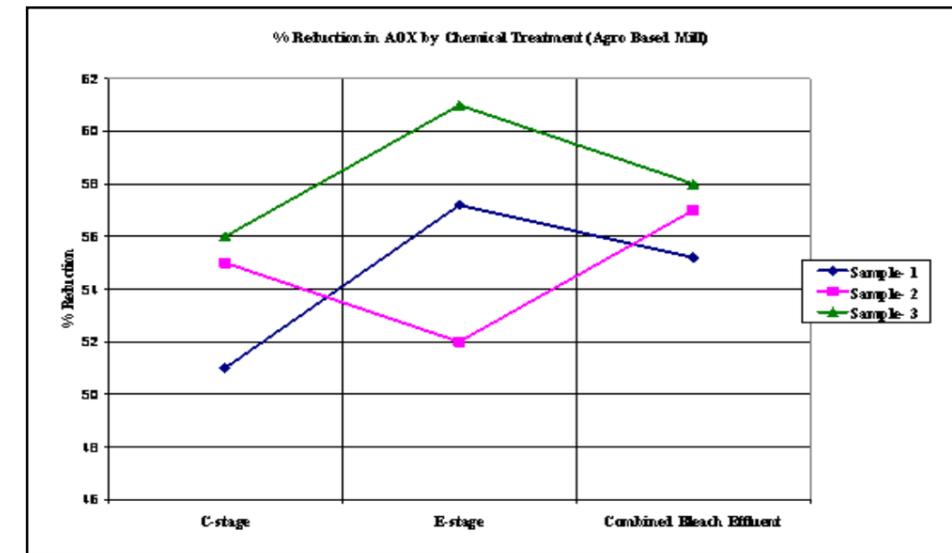


Fig. 5 Reduction % in AOX by Chemical treatment (Agro based mill)

E-stage effluent is reduced upto 73% (Milestone, 1988). AOX was reduced by 60 to 70% by this method, at 50°C, one hour reaction time, and a resultant bleach plant effluent pH of 8 to 9, which is still biologically treatable. Francis *et al.* (1998) studied in laboratory and reported that the chemical pretreatment reduced the AOX in the acid effluent by 50%. Francis also reported that the percent AOX reduction by combined chemical and biological treatment ranged from 53 to 59% depending on the operating conditions of the biological treatment plant. Laboratory studies show that the chemical treatment also results in reduction of toxicity potential 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.

capital investment are the major bottlenecks which restrict the Indian pulp and paper mills to adopt these new technologies. Thus an integrated approach with chemical treatment of segregated bleach plant effluent are required to be adopted by Indian mills to reduce the AOX level which will be cost effective and also the toxicity effect of bleach plant effluent.

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CONCLUSION

In the changed scenario with stringent norms and public awareness regarding environmental issues particularly control of discharge of AOX related compounds from pulp and paper mills is measure tasks for Indian mills. Most of the pulp and paper mills in developed countries have switched over to new fiber line with cleaner production techniques and improved bleaching practices. The scale of operation, use of mixed fibrous raw material and high

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