

Low Cost Treatment of Pulp and Paper Mill Wastewaters for Organochlorine Removal

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Abstract

Oxygen delignification process followed by ECF bleaching is the best suited technological option. But it becomes uneconomical for the smaller size pulp mills with capacity of 100-250 tpd. External treatment of the wastewater with suitable method might be the cost effective route to comply the regulations. The present paper deals with the findings of the laboratory scale study on pretreatment followed by biological oxidation process of $C_D + E_O$ stage wastewaters to contain the organochlorines. Pretreatment of the wastewaters with lime removes 30-41.6% AOX and 61.4% EOX with 54.2-71.4% mineralization of the AOX. Biological oxidation process removes 31-42% AOX further. The treated wastewater after the biological process is having very low level of toxicity; 93% of the EOX is removed. Pretreatment with lime removes significant amount of COD and colour. Caustic is less efficient in removing AOX, colour and COD. The treatment might be suitable for organochlorine removal in wastewaters of smaller size pulp mills provided the sludge generated in the treatment is disposed of in environmentally sound manner.

INTRODUCTION

Organochlorines are generated during bleaching of unbleached pulp with chlorine or its derivatives. Some of the organochlorine are toxic in nature. Total chlorine free bleaching (TCF) and Elementary chlorine free bleaching (ECF) are introduced in Europe and North America to eliminate or contain the release of organochlorines within an environmentally safe limit. Chlorine based bleaching is still dominant in majority of pulp mills in India. Though the intensity of pulp and paper mills in India is very thin as it is too scattered throughout the country, regulatory agencies are imposing stricter norms and have made a time bound programme to regulate the release of organochlorines.

Since the detection of dioxin and dibenzofuran in pulp and paper mill effluents in eighties, global attention has been drawn on the release and control of toxic pollutants in the pulp bleaching process with chlorine or chlorine derivatives.

The pulp and paper industry in India operates in an extremely complex situation, whereas the Western countries are relatively large in size, and utilize well specified raw materials and advanced production technology. Indian mills are smaller in size having production capacity ranging from 24,000 to 1,60,000 tonnes per year (in the category of large pulp and paper mills) in a single production site; use wide variety of raw materials such as bamboo, eucalyptus, and several tropical hardwoods such as subabool, casuarina, acacia, mango etc. and produce all ranges of products having high level of brightness.

These mills produce unbleached pulp of 18-24 kappa number and bleach the pulp mostly with chlorine and chlorine derivatives such as calcium hypochlorite, ClO_2 is mainly used as a polisher in the final stage(s) of bleaching to enhance the brightness of pulp.

The scale of operation and obsolescence of process technology are the two major factors for the high resource consumption. Though the intensity of pulp and paper mills in India is very thin as it is too scattered throughout the country, the industry is considered to be one of the major contributors of environmental pollution. Since the promulgation of comprehensive legislation in 1986 more and more stringency is being imposed on the industry to conserve the resources and reduce the environmental emission in line with the policy followed in the western world. The industry and regulatory agencies have mutually accepted a time bound programme to regulate the release of organochlorines measured through adsorbable organic halides (AOX).

Oxygen delignification process followed by ECF bleaching is the best-suited technological option. But it becomes uneconomical for the smaller size pulp mills with capacity 100-250 tpd. External treatment of the effluent with suitable method

might be the cost effective solution to bring down the adsorbable organic halide load to the desired level. Present paper deals with the laboratory scale findings on pretreatment and biological oxidation process to contain the AOX level in the bleach plant wastewaters.

MATERIALS AND METHODS

Materials

A laboratory scale treatment system was developed consisting of primary clarifier of 2.5 litre, aeration reactor of 2.25 litre and secondary clarifier of 0.9 litre. The wastewater was fed and sludge was recycled by Masterflex peristaltic pumps. The schematic diagram of the treatment system is given in Fig.1. C_D and E_O stage wastewaters and combined wastewaters before and after treatment were collected from integrated pulp and paper mills. The wastewaters and sludges were preserved below 4°C .

Analytical Methods

Adsorbable Organic Halides (AOX) was determined as per ISO Method No. 9562:1989 using Euroglas make AOX analyzer (Model No. ECS 2000). p-chlorophenol (SD Fine Chemicals, India) was used as the standard.

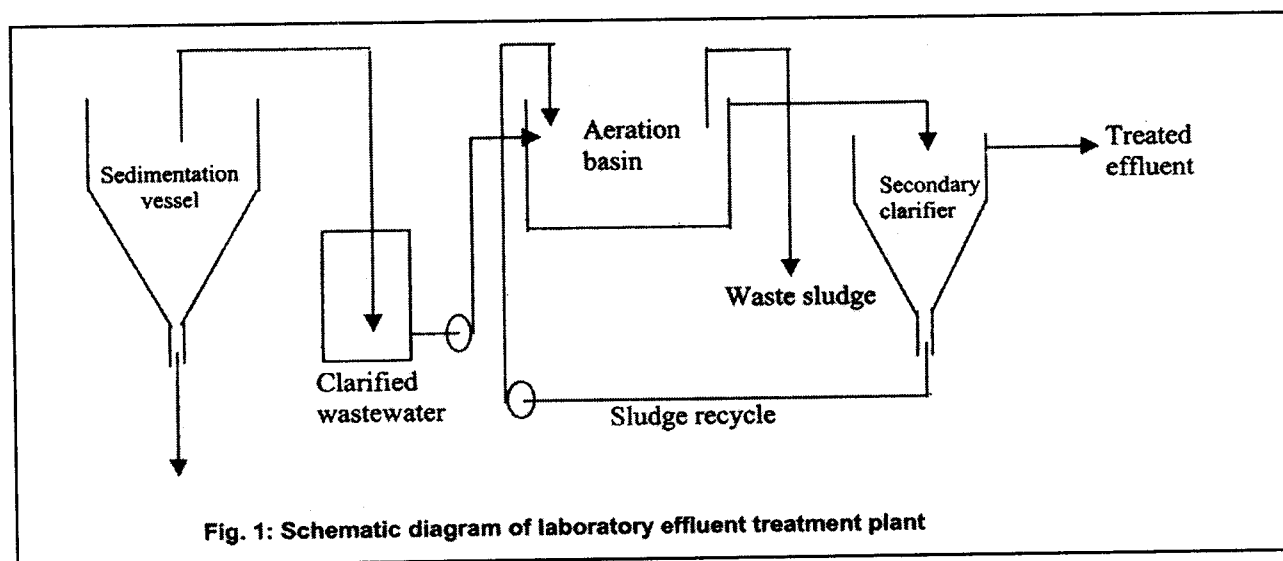


Fig. 1: Schematic diagram of laboratory effluent treatment plant

Extractable Organic Halides (EOX) was determined as per DIN 38409 Part 8 with Euroglas ECS 2000 analyzer using EOX cassette. Aldrin (Aldrich Chemical, USA) solution in n-hexane and hexadecane having a concentration of 10 mg/l was used as the standard.

Chloride was determined as per potentiometric method (APHA 4500 Cl D) using Orion 960 Autochemistry System, USA. Analytical grade NaCl of SD Fine Chemical was used as the standard.

Chemical Oxygen Demand (COD) was determined by open reflux method as per APHA method No. 5220D.

Biochemical oxygen demand (BOD₃) was determined at 27°C for 3 days as per IS method no. 3025 Part 44.

Colour was determined by spectrophotometric technique as per Hach method No. 8025. The pH of the wastewater was first adjusted to 7.6 by using H₂SO₄ or NaOH solution and filtered through Whatman filter No.1.

RESULTS AND DISCUSSION

Three integrated pulp and paper mills were

selected for the present study due to the variation in pulping raw material, cooking condition, bleaching sequence and wastewater treatment process. The bleaching sequence of the mills were as follows:

Mill A	C _D E ₀ DD
Mill B	C _D E ₀ HHD
Mill C	CE _p HHD

Mill A uses mostly wood based raw material and more ClO₂ in the bleaching process; Mill B uses more than 50% bamboo as raw material and Mill C uses mixture of raw material including mango. Brightness of the bleached pulp in these mills was in the range of 86-89° ISO. All the mills are equipped with primary and secondary wastewater treatment systems with activated sludge process. Mill C has the separate primary clarification for the pulp mill and paper machine wastewaters, and aerobic lagoon as part of secondary treatment system.

Laboratory scale study on AOX removal by conventional treatment process

Laboratory scale study was carried out with the combined wastewater of Mill A as the mill was near to the laboratory and transportation of the wastewater took less time. Lime for pH

Table1: AOX removal in the effluent treatment process (Lab scale study)

AOX								
Inlet to ETP (mg/l)	Primary clarifier overflow		Treated effluent		Primary sludge		Secondary sludge	
	Concn. (mg/l)	Removal (%)	Concn. (mg/l)	Removal (%)	Concn. (mg/kg)	Removal (%)	Concn. (mg/kg)	Removal (%)
11.47	8.06	29.7	4.85	57.6	1396	12.2	4824	2.0
9.85	7.49	24.0	5.22	47.0	1368	12.9	4684	2.9
9.81	7.47	23.9	4.56	53.5	1429	13.5	4982	3.1
Avg		25.9		52.7		12.9		2.7

correction and alum for coagulation was added in the laboratory during the time of study. AOX concentration in the combined wastewater was in the range of 9.81 to 11.47 mg/l (Table 1). Lime was added upto pH 7.5 and subsequently alum was added upto pH 7. Settling in the clarifier resulted in 25.9% AOX reduction on an average in the wastewater. AOX concentration in the sludge was 1368 to 1429 mg/kg and 12.9% of AOX of untreated wastewater was removed by adsorption in the primary sludge.

to be 1% (not given in the text). It is observed that 3% of total AOX reduction in the secondary treatment gets vaporized, 11.3% gets adsorbed with the sludge and rest 85.7% gets mineralized to inorganic chloride.

AOX reduction in the mills

AOX reduction was evaluated in three specified integrated mills. 13.6-23.3% of the AOX compounds in untreated wastewaters was observed to be removed during the primary

Table 2: AOX removal in the wastewater treatment process in integrated pulp & paper mills

Mill	AOX								
		Primary clarifier overflow		Treated effluent		Primary sludge		Secondary sludge	
	Inlet to ETP (mg/l)	Concn. (mg/l)	Removal (%)	Concn. (mg/l)	Removal (%)	Concn. (mg/kg)	Removal (%)	Concn. (mg/kg)	Removal (%)
Mill A	10.85	8.32	23.3	5.45	49.77	2313	13.48	3947	1.72
Mill B	21.83	17.80	18.5	10.49	51.95	1745	4.28	8851	2.67
Mill C	29.72	25.68	13.6	10.21	65.65	1321	1.73	4728	1.60

Active microorganism of the secondary treatment process of the Mill A was used in the laboratory scale biological treatment process for fast adaptation in the laboratory condition with the substrate. AOX reduction in the secondary treatment (based on concentration of AOX in the clarified wastewater) was 30.3 to 39.8% and the overall AOX reduction was 52.7% on an average. As precise estimation of the net biomass growth was not possible in the small laboratory scale reactor biomass growth was estimated theoretically to be 50% of the BOD₅ reduction in the aeration basin. AOX concentration in the secondary sludge was found to be in the range of 4684 to 4982 mg/kg and 2.7% (average) of the AOX in untreated wastewater was adsorbed in the secondary sludge. Purgable Organic Halide content in the C_p+E_o stage wastewater was found

clarification process (Table 2) More the usage of lime in the wastewater treatment process, more was the AOX removal in the primary treatment. Highest removal was noticed in the Mill A which used more ClO₂ and hence more lime for acid neutralization. AOX removal by adsorption alone with fibres, fines and fillers in mills was not significant enough as observed through the study of Mill B and C wastewaters. AOX concentration in primary sludge was in the range of 1321 to 2313 mg/kg of dry sludge and AOX removal through primary sludge ranged from 1.73 to 13.48% of the incoming load in the mills. In spite of the lowest AOX removal in the primary clarifier sludge in Mill C, highest overall AOX reduction indicates that reduction of AOX compounds in the secondary treatment is

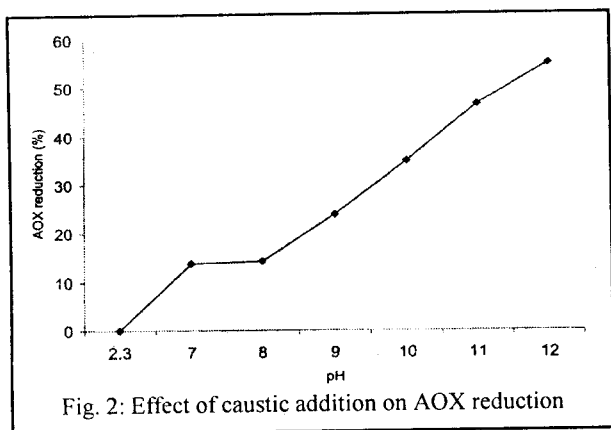


Fig. 2: Effect of caustic addition on AOX reduction

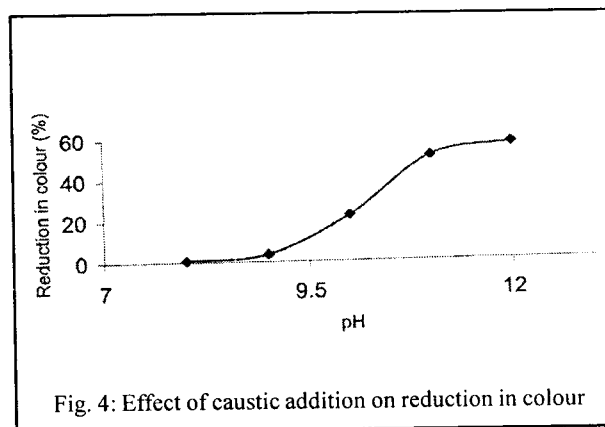


Fig. 4: Effect of caustic addition on reduction in colour

very high. It also points out that the AOX compounds removed in the primary clarification might also be reduced by biological treatment. It might be that the microbial mineralization of AOX is also higher in the aerobic lagoon which has also been reported by Hall and Randle (3).

colour and 83-86% COD in $C_D E_O$ HHD and CE_p HH sequence of bleaching of Indian raw materials. Hence treatment of these two stages appropriately

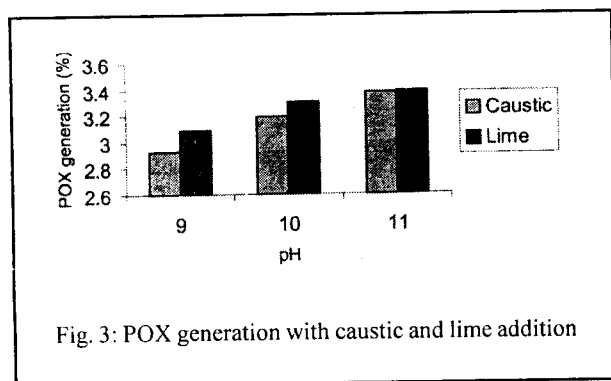


Fig. 3: POX generation with caustic and lime addition

Table 3: Effect of caustic addition on COD removal

pH after caustic addition	COD	
	Concn. (mg/l)	Redn. (%)
10	1035	10.6
11	1028	11.2

AOX concentration in the secondary sludge is highest in the Mill B (8851 mg/kg) whereas for Mill A and Mill C the concentration is in the range of 3947-4728 mg/kg. Morphology of microbial sludge in the activated sludge process and colloidal charge in the system have great role in the adsorption of organochlorine compounds. AOX removal through the secondary sludge is only 1.6 to 2.67%.

removes bulk of the pollutants.

Addition of alkali (caustic) to $C_D + E_O$ stage wastewaters

Chlorination and extraction stages are the major source of pollutant generation; combinedly they are responsible for 75-80% AOX, more than 99%

C_D and E_O stage wastewaters collected from Mill A were mixed in the proportion of 2:1. Caustic soda solution was added to make up the pH from 7 to 12.0. AOX reduction by caustic treatment is given in Fig.2. In the weak alkaline condition hydrolysis of chlorine bond in aliphatic and aromatic molecules was mild; about 24% at pH 9. Severity of the alkaline condition enhanced

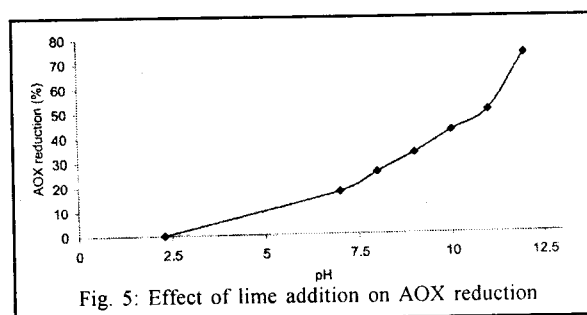


Fig. 5: Effect of lime addition on AOX reduction

the hydrolysis and steadily increased from 23.9 to 55.2% over the pH range of 9 to 12. Similar observations have also been reported by other researchers (4-6). Alkali addition resulted in release of POX (Purgable organic halide) compounds. Generation of POX varied from 2.93 to 3.38% of the incoming AOX in the wastewater (Fig.3).

Alkaline hydrolysis of chlorolignin, haloform

after pH 10.0 Maximum colour removal of 56.7% was observed at pH of 12 (Fig.4).

Effect of caustic addition on COD removal was studied at two pH levels 10 and 11. Caustic addition has very little effect on precipitating organic substances (Table 3) and hence COD removal.

Addition of lime to C_D+E_O stage

Table 4: Effect of lime addition followed by biological treatment on AOX removal (lab scale study)

S.No.	Inlet wastewater		Lime treatment				AOX removal		
	AOX (mg/l)	Cl (mg/l)	AOX in overflow (mg/l)	Cl in overflow (mg/l)	POX* (mg/l)	AOX in. sludge* (mg/l)	AOX in treated effluent (mg/l)	Lime treatment (%)	Overall (%)
Mill A wastewater (C _D +E _O in 2:1 proportion)									
1.	87	1610	59.1	1630	3.2	4.8	34.3	32.1	60.6
2.	105	1940	67.0	1967	4.6	4.8	47.7	36.0	54.6
Mill B wastewater (C _D +E _O in 2:1 proportion)									
3.	90	914	62.3	929	-	4.7	42.8	30.1	52.4

AOX concentration in lime sludge : Mill A 11824 mg/kg and Mill B 13423 mg/kg Mineralization of AOX : Mill A 71.4% and Mill B 54.2%

reaction of side chain precursors in lignin like methyl ketones which are formed during acidic chlorination step and reaction of lignin molecule with alkaline hypochlorite formed by conversion of residual chlorine with alkali (7-10) are the possible reasons of POX generation.

Caustic addition had insignificant effect on colour removal upto pH 9.0. It increased only

wastewaters

C_D and E_O stage wastewaters in the proportion of 2:1 was used in the study. Lime was added to makeup the pH from 7 to 12. It is the least expensive chemical, available in plenty and provides alkaline condition. AOX reduction steadily increased with lime addition. Even at pH 7.0, AOX reduction of 17.4% was observed which indicates that mixing of sectional wastewaters of bleach plant can help in partial reduction of organochlorines. AOX reduction was very high at pH 11 and above; 72.5% AOX can be reduced at high dose of lime at pH 12 (Fig. 5). Alkaline hydrolysis of chlorolignin, aliphatically bound chlorine and demethoxylated chlorocatechols resulted in partial mineralization of AOX compounds (4).

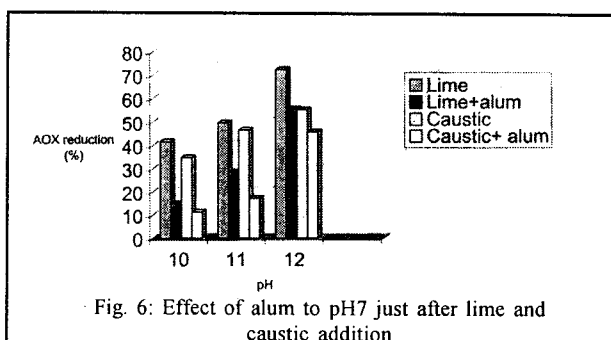


Fig. 6: Effect of alum to pH7 just after lime and caustic addition

Table 5: Effect of lime addition on EOX removal

Treatment method	EOX (mg/l)	Reduction (%)
Raw effluent	1.32	
Lime treatment	0.57	61.4
Biological treatment	0.093	83.7
Overall removal efficiency		93.0

AOX reduction with lime addition was observed to be higher at each pH level compared to that with caustic addition; lime not only provided

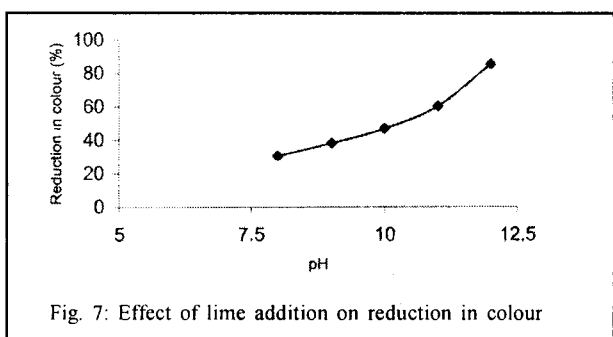


Fig. 7: Effect of lime addition on reduction in colour

alkali but Ca ion too which helped in better coagulation of hydrolyzed and un-hydrolyzed compounds. AOX reduction at pH 10 of the Mill A wastewater varied from 32 to 41.6% whereas for Mill B it was 30% (Table 4 and Fig. 5).

AOX concentration in the lime sludge was observed to be 11824 and 13423 mg/kg of dry sludge for Mill A and Mill B respectively which

Table 6: Effect of lime treatment on COD removal

pH after lime addition	COD	
	Concn. (mg/l)	Rendn (%)
10	741	29.4
11	595	43.3

COD of $C_D + E_O$ (2:1) wastewater: 1050 mg/l

corresponds to 5.1 and 5.2% AOX removal of the incoming AOX. Removal of organochlorines by both lime and alkali (caustic) is partially reversible. When alum was added to alkaline suspension made by lime or caustic to pH 10, 11 and 12 hydrolyzed or unhydrolyzed AOX compounds either in solution phase or in suspension get recombined or dissolved resulting in higher AOX concentration. Revesibility is higher at lower alkaline condition and stability of AOX removal is pronounced at higher pH (Fig.6).

Lime treatment releases some POX compounds. It varied from 3.1 to 4.4% over a pH range of 9 to 11 (Fig. 3). POX generation depends upon nature of raw material and process condition; for Mill A wastewater it varied from 3.3 to 4.4% of total AOX at pH 10. Marginally higher POX generation was noticed with lime in comparison to that with caustic addition at the three pH levels under study; it demonstrate that the POX generation is basically dependent upon alkaline condition.

Lime addition removes the AOX in two ways; partly by simple coagulation and partly by mineralization of the AOX compounds. Extent of mineralization were different for the wastewaters of two mills, for Mill A wastewater it was 71.4 and for Mill B it was 54.2%.

Secondary biological treatment was also carried out with the clarified wastewater of lime treatment after pH adjustment. Biological oxidation further removed 29-42% AOX based on the AOX concentration feed to aeration basin and 22.4-28.5% based on the AOX concentration of raw wastewater. Overall AOX reduction during lime and biological treatment was 57.6 and 52.4% for Mill A and B respectively.

Two step treatment involving lime addition followed by biological treatment significantly removes the toxic organochlorines measured through Extractable organic halides (EOX). EOX

compound are fat soluble and remain in fat tissues. Lime treatment alone and combinedly with biological treatment reduced EOX by 61.4 and 93% of the incoming wastewater respectively (Table 5).

Unlike caustic, lime had a great effect on colour and COD removal from bleach plant wastewaters. At pH 10 colour removal was more than 46% with lime addition whereas it was only 22.3% with caustic. More than 85% colour can be removed by lime addition at pH 12.0 (Fig. 7)

At two levels of pH 10 and 11 COD removal was appreciable with lime addition. At pH 11 it was more than 43.3% (Table 6) whereas with caustic addition it was restricted within 10-11. Hydrolysis of chlorolignins and coagulation are the predominant phenomena in case of lime addition to bleach plant wastewater. Hydrolysis takes place with caustic but monovalent sodium has limited role in coagulating hydrolyzed compounds.

CONCLUSION

Multipart study on AOX reduction of bleach plant wastewater reveals the following points: Both laboratory scale study Mill A wastewater and treatment in the commercial plant reduce 23.3-25.9% AOX during clarification; 12.9-13.48% AOX is adsorbed in the primary sludge, 49.77-52.7% AOX is removed in the entire treatment of Mill A wastewater and 1.72-2.7% of AOX is adsorbed in the secondary sludge. Fibres and fillers in pulp and paper mills has no significant role in separating the AOX compounds during primary treatments. 85% of the reduced AOX in the biological treatment gets mineralized and role of vaporization and adsorption is not significant. Aerobic lagoon reduces AOX compounds to a higher proportion than activated sludge process. Between caustic

and lime lime is more efficient removing AOX, colour and COD compounds; at pH 11 reduction of the three parameters are 49.7, 60 and 43.3% respectively. Separation of AOX compounds is relatively nonreversible with lime treatment compared to caustic under alum treatment.

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REFERENCES

1. Svenningsen N.W. *Proc. Tappi Environm. Con.*, 1031-1040 (1999).
2. Qionon H. and Koskivirta M. *Proc. Paperex*, New Delhi, 49-68 (1999).
3. Hall E.R. and Randle W.G. *Water Sci. Tech.* **26** (1-2), 387-396 (1992).
4. Dorica J. *J. Pulp Paper Sci.*, **18** (6), J 231-J 237 (1992).
5. Milosevich G.M. and Hill D.A. *Pulp paper Canada*, **93** (3), 61-67 (1992).
6. Fukui H., Barron B.S. and Matsukura M. *Tappi J.* **77** (1), 167-171 (1994).
7. Hrutfiord B.F. and Negri A.R. *Tappi J.* **73** (6), 219-225 (1990).
8. Amendola G., Berma D., Blosser R., LaFleur L, Mc Bride A., Thomas F., Tierman T. and Whitemore R. *Chemosphere*, **18**, 1181-88 (1987).
9. Chakrabarti S.K., Bhardwaj N.K., Roy M., Chandra S., Kumar S., Singh S. Bajpai P.K. and Jauhri, M.B. *Proc. 6th Inte. Asso. Water Quality Symp. on Forest Ind. Wastewaters*, Tampere, Finland, June 6-10, pp.393-396 (2003).
10. Chakrabarti S.K., Singh S., Chandra S., Roy M. and Bajpai P.K., *Proc. 7th Inte. Water Ass. Conf. on Forest Ind. Wastewaters*, Seattle, USA, June 1-4, pp. 1-11 (2003).