A critical review of the ability of biological treatment systems to remove chlorinated organics discharged by the paper industry

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Abstract

One of the principal problems facing the pulp and paper industry is the discharge of chlorinated organics into the environment. The fate of chlorinated organics produced during pulp bleaching with chlorine-based compounds in waste-water treatment systems is critically examined. Aerobic and anaerobic processes are capable of removing chlorinated organics to varying degrees of efficiency. However, the mechanism by which this removal occurs has not been identified precisely.

Nomenclature

AOX - adsorbable organic halide
BOD - biological oxygen demand
COD - chemical oxygen demand
D - Dalton
HMM - high molecular mass
HRT - hydraulic retention time
kD - kilodalton
LMM - low molecular mass
SRT - solids retention time
TOCl - total organic chlorine
TOX - total organic halide

Introduction

The effect of the pulp and paper industry on the environment is now being closely examined. Mills using chlorine-based compounds for bleaching, discharge chlorinated organics (primarily chlorinated lignin degradation products) into the environment. Some of these compounds may be toxic and mutagenic (Germgard et al., 1984; Kringstad and McKague, 1988) and may bioaccumulate in fish tissue (Renberg et al., 1980). But Craig et al. (1990) reported that the concentration of chlorinated organics discharged could not be related to effluent or sediment toxicity.

An increasingly attractive means to reduce the discharge of chlorinated organics, as measured by adsorbable organic halide (AOX) content, is to modify the bleaching process either by using oxygen delignification or by substituting chlorine dioxide for chlorine (Graves et al., 1993). These techniques serve to reduce chlorinated organics as well as BOD, COD, and toxicity (Germgard et al., 1984; Pryke, 1989; Singh, 1988). However, these process modifications are typically capital-intensive; mills will more likely rely on their presently-installed waste-treatment systems to remove the bulk of the chlorinated organics for the foreseeable future. The most common methods of waste treatment are biological systems such as aerated lagoons, activated sludge, and anaerobic technology.

In the United States, the only federal regulation by the Environmental Protection Agency for chlorinated organics is for the total amount of the 75 congeners of dibenzo-*p*-dioxin discharge to be less than 0.013 kg/t (Kinstrey, 1993). Several states have begun monitoring the discharge of AOX. Alabama requires pulp mills to report AOX each quarter when applying for waste-water treatment permit renewals, and Oregon requires discharge of less than 1.5 kg TOCl/t (Kinstrey, 1993).

Other countries have, however, passed regulations regarding the discharge of chlorinated organics into receiving waters. Canada regulates the discharge of AOX to 2.5 kg/t, and plans to decrease this limit to 1.5 kg/t by 1994 (Randle et al., 1991). Sweden will limit the discharge of TOCl to less than 0.01 kg/t by the year 2010 (Kinstrey, 1993).

With these regulations and concerns in mind, the efficacy of current biological treatment methods, such as aerated lagoons, activated sludge processes, and anaerobic processes, to remove chlorinated organics in the paper industry is critically examined herein. There is much conflict in the literature concerning how much AOX can be removed and what the mechanism may be.

Organic chlorine compound determination

There are several non-specific parameters that can be used to measure the amount of organically bound halogen. In the pulp and paper industry, almost all halogen measured is chlorine, with minor amounts of bromine present due to bromine-containing biocides used on the paper machine. Total organic halide (TOX) is termed a sum parameter test since it measures, without discrimination between specific organic compounds, all organic halogen compounds. In the pulp and paper industry, the bulk of the TOX is lignin degradation products from the pulping process to which chlorine has been added during the bleaching process. Although the carbon/chlorine ratio remains essentially constant through the biological treatment system (Aprahamian and Stevens, 1990), the amount of AOX ultimately discharged depends on many factors including wood source (less AOX is produced when hardwood rather than softwood is bleached; Tomar and Allen, 1991), use of oxygen prebleaching (Graves et al., 1993), and the amount of chlorine dioxide substitution (Barton and Drake, 1993).

Traditionally, TOX measurements involve the combustion of organic compounds dried onto cellulose filter paper in an oxygen atmosphere (Sjöström et al., 1985). The organic halide is con-

verted by the combustion process to chloride ion which is then measured by a specific ion electrode or a silver ion titration specific for chloride. The adsorbable organic halogen measures those organic compounds which can be adsorbed onto activated carbon; not all LMM compounds, such as chlorinated phenols, guaiacols, and veratroles, are completely adsorbed by activated carbon (Pellinen and Joyce, 1991). The activated carbon is burned and the organochlorine compounds are converted to hydrochloric acid which is absorbed in an aqueous solution and measured by microcoulometry. Compounds which are moderately volatile are also poorly characterised by AOX (Bryant and Amy, 1988).

A limitation in TOX (AOX) measurements is the problem with solid samples. Analysis of solid samples, such as waste-water sludges, requires the use of an extraction technique to solubilise the chlorinated compounds. Solvents such as diethyl acetate, ether, and octanol have been recommended to extract chlorinated phenolics from soil. However, even these solvents are not 100% effective at extracting chlorolignin compounds from soil (Bryant and Amy, 1988). An improved method is reported to be the extraction of the chlorinated compounds after acetylation (Brezny and Joyce, 1992).

Mechanism of AOX removal during biological treatment

Removal of AOX is thought to involve air stripping of volatiles (for example, chloroform), aerobic biodegradation of LMM chlorinated lignin, precipitation of HMM lignin degradation products (Severtson and Banjeree, 1993), and biosorption of chlorinated lignins onto settling biomass with subsequent degradation or dehalogenation in the benthic layer of the lagoon (Tomar and Allen, 1991; Bryant et al., 1988). The degradation of HMM chlorolignins also proceeds by light-induced photolysis (Caron and Reeve, 1992; Archibald and Roy-Arcand, 1993).

Bryant et al. (1988) have confirmed that chloroform is removed by volatilisation during aeration. However, only about 5% of the total AOX is removed by volatilisation (Bryant and Amy, 1989). Randle et al. (1991) reported that 67 to 96 % of the AOX removal is due to biodegradation. It has also been reported that less than 10% of the AOX is bound to the sludge (Randle et al., 1991; Ferguson, 1993). From analysis of core samples taken from the sludge in aerated lagoons, AOX levels in the water column were about seven times as high as the interstitial water associated with the sludge. This is most probably due to a combination of biosorption, lignin precipitation, and benthal dehalogenation (Bryant et al., 1988). They also estimated, based on material balances, 98% dehalogenation in the benthal layer of the lagoon. But Tomar and Allen (1991) performed a similar analysis and found only 25% removal in the benthal layer, and a higher AOX content in the overlying water as compared to the interstitial water. If the chlorinated compound is not degraded or dehalogenated, it may enter the terrestrial environment when a waste-water sludge is deposited in a landfill or spread on land.

Anaerobic dehalogenation is a reductive process which can use a chlorinated compound as an electron acceptor. Chlorine is removed from the compound and replaced by hydrogen. This process often yields compounds that are more susceptible to further biotransformations. Some chlorinated phenols can serve as both the electron donor and acceptor. Other compounds, however, require the addition of reducing equivalents. For most chlorinated compounds, the reductive dechlorination process proceeds in a stepwise fashion until all halogens are removed. It is important to note that reductive dehalogenation reactions are limited to

methanogenic microcosms and do not occur in sulphate-reducing microcosms (Suflita and Sewell, 1991). As the number of chlorine substituents increases, so does the electronegativity and, therefore, the susceptibility to reduction increases. Additionally, the removal of chlorine from an aromatic molecule is easier when the ring is also substituted with electron destabilising groups, such as methoxy and hydroxy groups (Sims et al., 1991).

Aerated lagoons

The standard configuration for aerated lagoons in the paper industry includes a basin with mechanical agitation, followed by several polishing basins which rely upon natural aeration. Most AOX removal occurs in the portion of the lagoon which receives mechanical aeration. Cook (1990) reported that 74% of the total AOX removal takes place in the aeration basin within the first 2.5 d. This observation was also confirmed by the work of Oleszkiewicz et al. (1992) and Tomar and Allen (1991). Oleszkiewicz et al.(1992) found no removal of AOX in the final polishing lagoon.

Unfortunately, information on the size of the lagoon, the energy supplied for aeration, and the dissolved oxygen profiles in the lagoon is rarely provided. The most often stated parameter for aerated lagoons is the retention time. This, however, is not enough to validate the mechanism of AOX removal. If dissolved oxygen profiles were available, it would be possible to determine if certain areas of the lagoon were anaerobic, and at what depth this change took place. The role of anaerobic dehalogenation could then be more closely analysed.

Overall removal of AOX in the aerated lagoon system varies from 15 to 50% of the total AOX (Oleszkiewicz et al., 1992; Randle et al., 1991; Tomar and Allen, 1991; Bryant and Amy, 1989). But, higher AOX removal is observed for LMM (< 1 kD) chlorinated compounds as compared to the total AOX, where molecular mass may range up to 100 000. Removals of 43 to 60% of LMM AOX have been reported (Tomar and Allen, 1991; Aprahamian and Stevens, 1990). This increase in removal efficiency is due to transport of LMM compounds through bacterial cell membranes, and the resulting biodegradation. Bryant and Amy (1989) have found a positive correlation between the presence of LMM chlorinated organics and acute and chronic toxicity. Only about a 20% reduction in AOX for HMM compounds has been observed (Aprahamian and Stevens, 1990). The reduction of some specific chlorinated organics (McKague et al., 1989, have identified over 300 compounds in bleach plant effluents and estimate this to be about 10% of the compounds which could be identified) by aerated lagoons is presented in Table 1.

The effectiveness of AOX removal also depends upon the effluent source. Stuthridge et al. (1991) found AOX removal to be different for chlorination and extraction stage effluents. A New Zealand mill treats its chlorination stage effluent in an aerated lagoon with an HRT = 4.4 d and its extraction stage effluent in an aerated lagoon with an HRT = 45 d. Table 2 presents the molecular mass distributions of AOX in treated and untreated effluents. System A, treating chlorination stage effluent, contained 57% of the AOX < 3 000 D, but only 7% of the AOX > 100 000 D. In comparison, System B, treating extraction effluent, had 31% of the AOX with a molecular mass < 3 000 D and 26% > 100 000 D. After aerobic treatment, no significant change occurred in the molecular mass distribution of System A indicating a uniform degradation of chlorinated matter regardless of the molecular mass. For System B, however, there was a decrease in the less than 3 000 D range, but otherwise remained constant. As expected from inspection of

TABLE 1
CHLORINATED ORGANIC COMPOUNDS REMOVED BY AERATED LAGOON TREATMENT. (D+C)EODED BLEACHING OF PINE. (GERGOV ET AL., 1988)

	Removal (%)
AOX	32
Chlorinated phenols	43
Chlorinated guaiacols	70
Chlorinated catechols	15
Chlorinated vanillins	89
Combined chlorinated phenols, guaiacols, catechols and vanillins	54

TABLE 2
MOLECULAR MASS DISTRIBUTION OF AOX IN UNTREATED AND TREATED WASTE WATERS (STUTHRIDGE ET AL., 1991)

	Molecular mass	% of total AOX C-Stage	% of total AOX E-Stage
Before treatment	< 3 kD	57	31
	3 - 10 kD	20	17
	10 - 30 kD	9	9
	30 - 100 kD	7	17
	> 100 kD	7	26
After treatment	< 3 kD	57	19
	3 - 10 kD	18	24
	10 - 30 kD	7	11
	30 - 100 kD	7	19
	> 100 kD	11	27

kD = kilodalton

TABLE 3
REPORTED REMOVALS OF INDIVIDUAL CHLORINATED ORGANICS BY ACTIVATED SLUDGE

	Rempel et al., 1992	Wilson et al., 1991	Leuenberger et al., 1985
Dichlorophenol	n.r.*	78	27
Trichlorophenol	60	51-69	28
Tetrachlorophenol	86	86-100	33
Pentachlorophenol	50	50-80	26
Dichloroguaiacol	n.r.	67-97	54
Trichloroguaiacol	93	18-97	18-36
Tetrachloroguaiacol	99	59-99	13
Dichlorocatechol	n.r.	37	n.r.
Trichlorocatechol	95	63-95	n.r.
Tetrachlorocatechol	90	59-90	n.r.
OVERALL	89	n.r.	n.r.

n.r. = not reported

the molecular mass distribution, System A removed 65% of total AOX, while System B showed no significant AOX reduction.

The effect of seasonal variations on AOX removal efficiency appears to depend upon the individual mill. Cook (1990) observed no seasonal variation at Espanola, Ontario, Canada. However, Bryant and Amy (1989) observed a greater removal of TOX in spring due to a lower temperature when compared to summer. At a lower temperature, they asserted that the quantity of TOX adsorbed by the biomass increases (Bryant and Amy, 1989). Of the AOX removed, the LMM fraction removal was highly dependent on seasonal variation, but the HMM fraction was only dependent on wood source (Bryant et al., 1988). Randle et al. (1991) have demonstrated that removal efficiency for COD is increased at a lower temperature. Bryant and Amy (1989) have shown chlorinated organic removal to track that of organic carbon for both the total and the LMm fractions.

Activated sludge

The perceived effectiveness of AOX removal by activated sludge systems is conflicting. Wilson and Holloran (1991) reported a much higher quantity of AOX removed when compared to aerated lagoons. Rempel et al. (1992) stated that AOX removal efficiency for activated sludge and aerated lagoons is identical. In these two studies, the per cent AOX removal ranged from 14 to 65%. This range brackets the removal efficiency for AOX in aerobic lagoons. Thus, the removal efficiency between different systems is not disputed, but the perception of the significance of AOX removal in activated sludge processes when compared to an aerated lagoon differs between observers.

Rempel et al. (1992) found that the removal of chlorinated phenolics is enhanced if the HRT is greater than 9 h. They state that, at a high solids retention time (SRT), the reactor experiences nutrient-limiting conditions and there is more time for the bacteria to acclimate to compounds which are difficult to degrade. However, in order for the activated sludge system to operate properly, the HRT must be increased with increasing SRT. Rempel et al. (1992) reasoned that the effect caused by changes in HRT is a covariate of changes caused by SRT. Also, the performance of systems with an SRT of more than 10 d was better than those with an SRT of less than 10 d. Similar performance results were found to apply to AOX. The increase in chloro-organic removal efficiency as both HRT and SRT increase is explained if biodegradation is the major pathway. The longer the compounds are retained in the treatment system, the greater the chance that the bacteria can acclimate and use the chloro-organic compounds which are difficult to degrade, thus increasing the removal of AOX. Removal of AOX is not likely to be caused by anaerobic dehalogenation because less than 10% is associated with the sludge and a high degree of aeration is supplied to the activated sludge reactor. However, neither the actual system design parameters nor the dissolved oxygen profile in the aeration tank were specified.

Randle et al. (1991) reported an average AOX reduction of 32% in an activated sludge system. The low AOX removal efficiency as compared to an aerobic lagoon with the same SRT suggests that the HRT, rather than the SRT, may control treatment effectiveness. Additionally, they found that the activated sludge system operated best at 25°C.

The removal efficiency for individual chlorinated organics ranged from 18 to 100% (Table 3). System operating temperature had no effect on effectiveness, but approximately 5% of the chlorinated phenolic material became associated with the waste biosludge (Randle et al., 1991). Chlorinated organic or AOX

removal was not affected by the use of pure oxygen, as compared to air, for system aeration (Wilson and Holloran, 1991; Rempel et al., 1992).

Anaerobic processes

The potential application of anaerobic technology in the pulp and paper industry has increased as the waste streams have become more concentrated due to efficient water recycling (Lettinga et al., 1991). At this time, anaerobic systems have found greater applicability with semi-chemical pulp and paper effluents (Wilson et al., 1988), recycled fibre effluents (Winslow, 1989), and evaporator condensates (Walters et al., 1988). Laboratory- and pilot-scale anaerobic systems have shown that a greater AOX removal efficiency is possible, compared to an aerobic system.

One of the major hindrances to the anaerobic treatment of bleach plant effluent is the inhibitory effect the waste water has on the methanogenic bacteria. Parker et al. (1991) found kraft bleach plant effluent to be non-inhibitory at levels as high as 95% v/v in a high-rate anaerobic reactor. However, Hall and Cornacchio (1988) reported a maximum ratio of 60% v/v to yield a non-significant inhibition of methane production. Ferguson (1993) experienced toxicity of bleaching waste waters to anaerobic organisms at a 85% v/v ratio. Parker et al. (1991) found that as the volumetric fraction of bleach plant effluent increased, lag time at start-up increased and the conversion of organic material to methane decreased. This trend was found in both chlorination (C) and extraction (E) stage effluent as well as whole mill effluent. At similar AOX concentrations, the C-stage effluent was more inhibitory than the E-stage effluent. This was due to the large quantity of LMM compounds in the C-stage effluent. Nilsson and Strand (1993) report that a 40% reduction in AOX is possible when up to 72% of the COD is E-stage effluent.

Parker et al. (1991) also found a statistically significant difference in the AOX removal efficiency of anaerobic reactors with and without methanol and ethanol added as cosubstrates. For reactors with HRTs from 6 to 48 h, AOX decreased 51.7 to 62.6% in cosubstrate supplemented reactors, while those without cosubstrate only removed 48.5 to 59.2%. These results were obtained in reactors where the volumetric fraction of waste water was 80% and the remaining 20% was the nutrient buffer. Cosubstrate addition did not significantly affect the removal of LMM AOX. However, as the HRT increased from 6 to 48 hours, AOX removal of LMM compounds increased from 67.3 to 78.3%. As the per cent waste water present in the reactor was increased to 95%, the AOX removal efficiencies decreased slightly.

An alternative to strict anaerobic treatment is anaerobic treatment of waste waters followed by an aerobic process. A full-scale system of this nature, the Enso-Fenox process, was tested in 2 Finnish mills (Wilson and Holloran, 1991). Hakulinen et al. (1981) reported a 77% decrease in chlorophenolics by a pilot-scale version of the Enso-Fenox process. Biodegradation of chlorophenolics was the suspected removal mechanism since an insignificant quantity of the chlorinated compounds was associated with the anaerobic sludge. Biosorption appeared to have a greater impact in the aerobic reactor that follows the anaerobic unit, where 25 to 33% of the soluble AOX could be accounted for on the biosolids (LaFond and Ferguson, 1991). Biodegradation is supported by a 40% decrease in the removal of chlorophenolics as the hydraulic loading was increased from 1.5 to 8 reactor volumes per day (Hakulinen et al., 1981). Ferguson (1993) demonstrated that an additional 5 to 8% AOX is removed if an anaerobic stage is followed by an aerobic stage.

AOX removal efficiencies of 20 to 30% and chlorinated organic removal efficiencies of 64 to 94 % are possible with a hydraulic retention of only 7 h (Boman and Frostell, 1988; Parker etial., 1993). This result is comparable to an aerated lagoon with a retention time of 7 d. If the HRT was increased to 24 h and the SRT was at least 100 d, AOX removal efficiencies as high as 68% were possible in laboratory-scale systems (Parker et al., 1991). A higher AOX removal efficiency was possible in systems treating kraft bleach plant effluent than in sulphite effluent (Wilson and Holloran, 1991).

Randle et al. (1991) reported a 56% decrease in AOX and an 83% decrease in chlorinated phenolics by a "facultative system," i.e. an anaerobic stage followed by an aerobic stage. These removal efficiencies are higher than the corresponding values for both aerobic lagoons and activated sludge systems. The removal efficiencies for both AOX and chlorophenolics increased with increasing temperature in the facultative system. This response was due to the higher temperature optimum of methanogenic bacteria. However, Saunamäki et al. (1991) did not report this same improvement in removal efficiency for AOX. They observed that little BOD remained after aerobic treatment. The anaerobic system may have been nutrient-limited and unable to dehalogenate the chlorinated compounds because of metabolic deficiencies.

In a laboratory study conducted by Prasad and Joyce (1993), an aerobic lagoon was followed by an anaerobic reactor. The aerobic stage removed a maximum of 21% AOX at either 4, 5, or 6 d retention time. The following anaerobic stage, at a 20 d HRT, removed an additional 36% of the AOX for an overall removal of 46% of total AOX. An HRT of 10 d in the anaerobic stage provided adequate AOX removal and was more economically feasible. The systems involving an anaerobic stage followed by an aerobic stage were more efficient because of an increase in the percentage of LMM compounds present after anaerobic treatment (Prasad and Joyce, 1993). This allowed for a higher removal in the following aerobic stage. This system had the highest percentage removal of AOX of any of the systems examined.

Conclusions

Concern about the effect of chlorinated organics on the environment has stimulated a great deal of research in the field of biological treatment and AOX reduction. Process modifications such as oxygen delignification and chlorine dioxide substitution can substantially reduce AOX. However, the high capital costs which accompany such modifications make the use of external, biological treatment systems more attractive, particularly since these systems are already installed.

Two main aerobic systems have achieved widespread acceptance: aerobic stabilisation basins and activated sludge plants. Both of these systems reduce AOX to some degree. Activated sludge plants generally remove a greater percentage of AOX than aerobic lagoons. However, the ability of each system to remove specific chlorinated organics varies greatly. The reason for this variability has not been adequately explained. Probably of prime importance is the design and operation of the system. For example, the dissolved oxygen profile throughout the system may influence the relative magnitude of apparent AOX removal because low dissolved oxygen (or anaerobic) conditions favour anaerobic dehalogenation.

Anaerobic treatment can also reduce AOX. Anaerobic metabolic pathways are better able to act on chlorinated organics. Systems which combine anaerobic and aerobic processes can realise the benefits of each. Thus, the reduction of AOX is

generally greater and is accompanied by a high removal of BOD and toxicity. More work is needed in this vital area to determine the optimal proportion of aerobic and anaerobic treatment. However, neither aerobic nor anaerobic systems appear able to substantially remove HMM AOX.

The proposed mechanisms for AOX removal in biological treatment systems are primarily theoretical. There is a great deal of anecdotal evidence supporting the various theories, but there is very little substantive evidence. Until the inter-related factors of system design and operation are better understood, attempts to optimise AOX removal from biological treatment systems will not be realised.

References

APRAHAMIAN, E (Jr.) and STEVENS, S (1990) The characterization of organochlorine compounds (AOX) in conventional and modified kraft mills. *TAPPI Pulp. Conf. Proc.* Toronto, Ontario, Canada October 14-17 **1** 209-215.

ARCHIBALD, F and ROY-ARCAND, L (1993) Effects of time, daylight, and settling pond microorganisms on the high molecular weight fraction of kraft bleachery effluents. *TAPPI Environ. Conf. Proc.* Boston, MA March 28-31 **1** 125-129.

BARTON, DA and DRAKE, EP (1993) Impact of increased chlorine dioxide substitution on the biotreatability of chlorinated organic compounds. *TAPPI Environ. Conf. Proc.* Boston, MA March 28-31 **2** 591-599.

BOMAN, B and FROSTELL, B (1988) Some aspects on biological treatment of bleached pulp effluents. *Nordic Pulp and Paper Res. J.* **1** 13.

BREZNY, R and JOYCE, T (1992) Extraction of chlorocatechols from soil after acetylation. *Chemosphere* **24**(8) 1031.

BRYANT, CW, AMY, GL, NEILL, R and AHMAD, S (1988) Partitioning of organic chlorine between bulk water and benthal interstitial water through a kraft mill aerated lagoon. *Water Sci. Technol.* **20**(1) 73.

BRYANT, CW and AMY, GL (1988) Organic halide in kraft mill wastewaters: Factors affecting in-mill formation and removal by biological treatment. *TAPPI Environ. Conf. Proc.* Charleston, SC April 18-20, **1** 435.

BRYANT, CW and AMY, GL (1989) Seasonal and in-mill aspects of organic halide removal by an aerated stabilization basin treating a kraft mill wastewater. *Water Sci. Technol.* **21**(4/5) 231.

CARON, RJ and REEVE, DW (1992) Environmental photolysis of chlorinated organic matter discharged in kraft pulp bleaching effluents. *Pulp and Paper Canada* **93**(8) 24.

COOK, CR (1990) Organochlorine discharges from a bleached kraft mill with oxygen delignification and secondary treatment. *Pulp and Paper Canada* **91**(8) 71.

CRAIG, GR, ORR, PL, ROBERTSON, JL and VROOMAN, WM (1990) Toxicity and bioaccumulation of AOX and EOX. *Pulp and Paper Canada* **91**(9) 39.

FERGUSON, JF (1993) Anaerobic and aerobic treatment for AOX removal. *TAPPI Environ. Conf. Proc.* Boston, MA March 28-31 **2**, 857-866.

GERGOV, M, PRIHA, M, TALKA, E, VALTTILA, O, KANGAS, A and KUKKONEN, K (1988) Chlorinated organic compounds in effluent treatment at kraft mills. *TAPPI Environ. Conf. Proc.* Charleston, SC April 18-20, **1** 443.

GERMGARD, U, KARLSSON, R-M, KRINGSTAD, KP, DE SOUSA, F and STROMBERG, LM (1984) Oxygen bleaching and its impact on the environment. *TAPPI Oxygen Delignification Symp. Proc.* San Francisco, CA November 15-16, **1** 99.

GRAVES, JW, JOYCE, TW and JAMEEL, H (1993) Effect of chlorine dioxide substitution, oxygen delignification and biological treatment on bleach plant effluent characteristics. *TAPPI J.* **76**(7) 153.

HAKULINEN, R, SALKINOJA-SALONEN, MS and SAXELIN, M-L (1981) Purification of kraft bleach effluent by an anaerobic fluidized bed reactor and aerobic trickling filter at semi-technical scale (Enso-Fenox). *TAPPI Environ. Conf. Proc.* New Orleans, LA April 27-29, **1** 197.

HALL, ER, CORNACCHIO, L-A (1988) Treatability Studies of Canadian Pulp and Paper Wastewaters. Environment Canada Report WTC-BIO-01-1988, Burlington, Ontario.

KINSTREY, RB (1993) An overview of strategies for reducing the environmental impact of bleach plant effluents. *TAPPI J.* **76**(3) 105

KRINGSTAD, KP and MCKAGUE, AB (1988) Bleaching and the environment. *TAPPI Int. Pulp Bleach. Conf. Proc.* Orlando, FL June 5-9, **1** 63.

LAFOND, RA and FERGUSON, JF (1991) Anaerobic and aerobic biological treatment processes for removal of chlorinated organics from kraft bleaching wastes. *TAPPI Environ. Conf. Proc.* San Antonio, TX April 7-10, **2** 797.

LETTINGA, G, FIELD, JA, SIERRA-ALVAREZ, R, VAN LIER, JB and RINTALA, J (1991) Future perspectives for the anaerobic treatment of forest industry wastewaters. *Water Sci. Technol.* **24**(3/4) 91.

LEUENBERGER, C, GIGER, W, CONEY, R, GRAYDON, JW and MOLNAR-KUBICA, E (1985) Persistent chemicals in pulp mill effluents: occurrence and behavior in an activated sludge treatment plant. *Water Res.* **19**(7) 885.

McKAGUE, AB, JARL, M and KRINGSTAD, KP (1989) An up-to date list on compounds identified in bleachery effluent as of January 1989. SSVL Miljö 90: Subproject "Bleaching", preprint from the *TAPPI Int. Wood Pulp. Chem. Conf. Proc.* May 22 -25, 1990, Raleigh, NC **1**.

NILSSON, B and STRAND, O (1993) Anaerobic treatment of evaporation condensate in combination with caustic extraction liquor from a pulp industry. *TAPPI Environ. Conf. Proc.* Boston, MA March 28-31 **1** 179.

OLESZKIEWICZ, JA, TREBACY, W and THOMPSON, DB (1992) Biological treatment of kraft mill wastewaters. *Water Environ. Res.* **64**(6) 805.

PARKER, WJ, HALL, ER and FARGUHAR, GJ (1991) Dechlorination of segregated kraft mill bleach plant effluents in high rate anaerobic reactors. *TAPPI Environ. Conf. Proc.* San Antonio, TX April 7-10, **2** 787.

PARKER, WJ, HALL, ER and FARQUHAR, GJ (1993) Assessment of design and operating parameters for high rate anaerobic dechlorination of segregated kraft mill bleach plant effluents. *Water Environ. Res.* **65**(3) 264.

PELLINEN, J and JOYCE, T (1991) The use of Schöniger combustion and ion selective electrode in TOCl determination. *Paperi ja Puu* **73** (5) 527.

PRASAD, DY and JOYCE, TW (1993) Sequential treatment of El stage kraft bleach plant effluent. *Bioresource Technol.* **44** 141.

PRYKE, DC (1989) Substituting chlorine dioxide for chlorine. *TAPPI J.* **72**(10) 154.

RANDLE, WG, HALL, ER and McKINLEY, AY (1991) Optimization of biological treatment systems for enhanced removal of AOX and chlorophenolic compounds. *TAPPI Environ. Conf. Proc.* San Antonio, TX April 7-10 **1** 433.

REMPEL, W, TURK, O and SIKES, JEG (1992) Side-by-side activated sludge pilot plant investigations focusing on organochlorines. *J. Pulp Paper Sci.* **18**(3) J77.

RENBERG, L, SVANBERG, O, BENGTSSON, B-E and SUNDSTRÖM, G (1980) Chlorinated guaiacols and catechols: bioaccumulation in bleaks. *Chemosphere* **9**(3) 143.

SAUNAMÄKI, R, JOKINEN, K, JÄRVINEN, R and SAVOLAINEN, M (1991) Factors affecting the removal and discharge of organic chlorine compounds at activated sludge treatment plants. *Water Sci. Technol.* **24**(3/4) 295.

SEVERTSON, SJ and BANJEREE, S (1993) The sorption of organics by pulp-derived solids. *TAPPI Environ. Conf. Proc.* Boston, MA March 28-31 **1** 97.

SIMS, JL, SUFLITA, JM and RUSSELL, HH (1991) Reductive dehalogenation of organic contaminants in soils and ground water. Ground Water Issue USEPA, EPA/540/4-90/054, January.

SINGH, A (1988) Mechanisms of reactions of chlorine, chlorine dioxide and nitrogen dioxide. *TAPPI Int. Pulp Bleach. Conf. Proc.* Orlando, FL June 5-9, **2** 85.

SJÖSTRÖM, L, RÅDESTRÖM, R, CARLBERG, G and KRINGSTAD, A (1985) Comparison of two methods for the determination of total organic halogen (TOX) in receiving waters. *Chemosphere* **14**(8)

1107.

SUFLITA, JM and SEWELL, GW (1991) Anaerobic biotransformation of contaminants in the subsurface. Environmental Research Brief, U.S. EPA, EPA/600/M-90/024, February.

STUTHRIDGE, TR, CAMPIN, DN, LANGDON, AG, MACKIE, KL, MCFARLANE, PN and WILKINS, AL (1991) Treatability of bleached pulp and paper mill wastewaters in a New Zealand aerated lagoon treatment system. *Water Sci. Technol.* **24**(3/4) 309.

TOMAR, P and ALLEN, DG (1991) Removal of organochlorines from kraft pulp mill effluent by an aerated lagoon. *Water Poll. Res. J. Canada* **26**(1) 101.

WALTERS, JG, KANOW, PE and DALPPE, HL (1988) A full-scale anaerobic contact process treats sulfite evaporator condensate at Hannover Papier, Alfred, Germany. *TAPPI Environ. Conf. Proc.* Charleston, SC April 18-20, **1** 309.

WILSON, DG and HOLLORAN, MF (1991) Decrease of AOX with various external effluent treatments. CPPA 77th Annual Meeting Technical Section, Preprints "b", Montreal, Quebec, Jan 31 - Feb 1, B281.

WILSON, RW, SCHNEIDER, E and FRENETTE, EG (1988) Anaerobic / aerobic treatment of CTMP and NSSC wastewaters. *TAPPI Environ. Conf. Proc.* Charleston, SC April 18-20, **1** 315.

WINSLOW, FB (1989) Operating experiences with an anaerobic / aerobic treatment system. *TAPPI Environ. Conf. Proc.* Orlando, FL April 17-19, **1** 465.