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DECREASE OF AOX WITH VARIOUS EXTERNAL EFFLUENT TREATMENTS

Some suggestions for discharge guidelines

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DURING THE LAST DECADE much of the concern over effluent emissions from the pulp and paper industry has shifted from the traditional parameters of BOD_5, TSS and color to chlorinated organic compounds.

In particular, the toxicity and effect of discharges of chlorinated dibenzodioxins and furans have been of concern as has the entire range of chlorinated organic compounds measured variously as AOX, TOX or TOCl. Governmental, academic and industrial groups have responded to this concern in a number of ways. Industry, its research agencies, and academia have sponsored research into methods of decreasing organochlorine discharges both through internal process measures, and external treatment measures.

Government has responded by proposing and/or implementing discharge guidelines on dioxins and furans, in particular, and on discharges of organochlorine as measured by the bulk parameters of AOX or TOCl.

A review is provided herein which describes the various external treatment measures that have been tested or implemented either on bench, pilot or full scale and their efficiency at removing AOX/TOCl/TOX in general, individual chlorinated organics, or various molecular weight fractions of organically-bound chlorine.

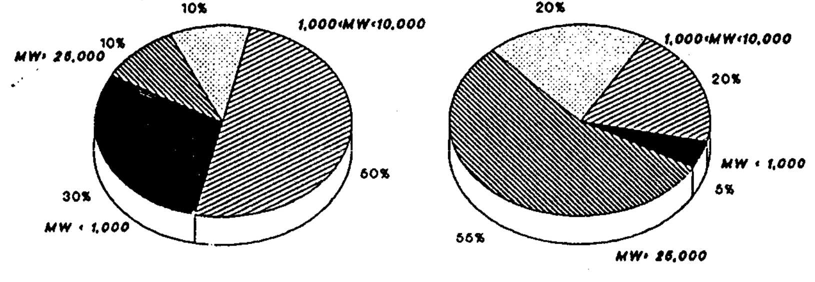
Further, the selectivity of removal of individual components of AOX and in turn their portion of the total toxicity of the effluent is reviewed with respect to the value of the use of bulk organochlorine parameters (AOX,TOX,TOCl) for regulating pulp and paper effluent discharges.

CHARACTERIZATION

The ability of various treatment techniques to reduce AOX in bleached pulp mill effluents effectively is related directly to the composition of the AOX. AOX is often described in terms of the individual compounds which comprise AOX [1] or in terms of the molecular weight (MW) distribution of the organically-bound chlorine in spent bleaching liquors [2].

A detailed list of individual compounds which compose pulp mill effluent has been reported by Suntio [1] while the MW distribution of organically-bound chlorine in chlorination and extraction liquors has been reported in some detail by Kringstad and Lindstrom [2], Fig. 1. In alkali extraction liquors 95% of the organically-bound chlorine is of relatively high MW (>1000) while in spent chlorination liquor only 70% of the organically-bound material is relatively high MW [2].

The composition of the high MW fraction is not well known and is considered by some authors to be biologically inactive. However, there is some evidence that the high MW compounds slowly degrade in the environment to form lower MW and more toxic compounds such as chlorinated catechols, guaiacols and veratrols [3,4]. The low MW fraction is known to contain many of the more degradable but most toxic chlorinated organics, in particular, chlorophenols and chlorinated organic acids.



SPENT CHLORINATION LIQUOR

SPENT ALKALI LIQUOR

FIG. 1. MOLECULAR WEIGHT DISTRIBUTION OF ORGANICALLY-BOUND CHLORINE.

The key to achieving high AOX removal efficiency is not only to treat the easily degradable, lower MW compounds, but to treat effectively the slower degrading high MW compounds, which are present in large proportions in the chlorination stage and, in particular, in the alkali stage spent liquors. Moreover, although alkali effluents are typically more toxic than chlorination stage effluents [2], the chlorination effluents typically have higher volumetric flow rates and hence there is a need to treat both streams to reduce effluent toxicity. Hall [5], in a study of four bleached kraft mills, reported that the bleach plant alkaline filtrates contribute 33 to 55% of the total effluent organochlorine load while the chlorination stage filtrate contributes 36 to 66% of the load.

The following review provides a summary of external treatment methods for bleach plant effluent AOX reduction and their specificity to AOX, chlorophenol or MW fraction removal.

EXTERNAL TREATMENT

Ultrafiltration: Realization that pulp and paper bleach plant effluents contain a high MW fraction that is not amenable to biological treatment [2,6,7] has in part led to more frequent consideration of ultrafiltration as an intermediate treatment step in a combined physical/biological treatment process. Several authors have cited ultrafiltration as a promising method for selectively treating spent bleach plant filtrates for organochlorine removal [6,8,9,10,11,12,13,14,15] either as a pretreatment or treatment step.

Ultrafiltration has been reported to remove from 50 to 99.8% of AOX or organic chloride from E-stage bleach plant filtrates [6,9,10,12,13,15] and has been used at full scale in Japan for several years [16]. Typical operating conditions are a flux of 0.03 to 0.40 m^3/m^2,h [6,9,13,15]. However, removal efficiencies when treating total mill effluents are markedly less, ranging from 20 to 45% [6,8,10,13].

Further, removal efficiencies for the lower MW chlorinated phenolics, the most toxic component of the AOX, are low [15,17]. Hence, it has been suggested that ultrafiltration may best be applied selectively to the relatively high MW bleach plant alkali stream as part of a combination treatment process. Combinations of ultrafiltration and biological treatment are reported to remove 62 to 90% of AOX.

In particular, removal efficiencies of 70 to 90% are reported for ultrafiltration and anaerobic biological treatment [6], 70% for ultrafiltration and fungal treatment, [13] 70 to 85% for ultrafiltration plus anaerobic/aerobic [13] and 62% for ultrafiltration plus anaerobic/aerobic treatment [10].

Chemical precipitation: Chemical precipitation of chlorinated organic material by iron and or aluminum salts has been reported as a potential AOX removal system [10]. Organic matter from chlorination and extraction stages has been successfully precipitated, on bench scale, using polyethyleneimine (polyimine). AOX removal efficiencies for treatment of bleach plant effluents range from 50 to 73% for alkaline stage liquors and 54 to 84% for the chlorination stage effluents [18,19]. A full-scale unit is currently operating on the effluent discharge of a 150-t/d German sulphite pulp mill [18].

An alternative lignin precipitation process is the lignin removal process (LRP) [20] which uses calcium oxide and polymer to precipitate lignin in a primary clarifier. The process itself operates on the principle of precipitation of organic waste matter upon addition of acidified fibre sludges. Pilot plant trials at bleached kraft pulp mills have resulted in TOCl removal efficiencies of 30 to 70% depending upon the wood furnish used in the pulp operation. Chlorinated phenolics were removed with an efficiency of 32 to 59% (also dependent on the wood furnish). LRP has been promoted as an attractive pretreatment alternative for biological treatment because of its ability to eliminate most of the high MW organically-bound chlorine, its small chemical requirements and its stable precipitate [21].

Ion exchange: Pilot and full-scale trials of an ion exchange effluent treatment system produced removal efficiencies of greater than 99% for chlorinated phenols and guaiacol [22,23]. In the ion exchange process the C- and E-stage effluents are acidified then treated continuously with the ion exchange resin with some of the effluent recycled for backwash of the filters and resin beds. The high removal efficiencies are somewhat mitigated by reported technical difficulties [24].

Oxidation: Ultrasonic oxidation of bleach plant effluent has been reported to remove, during simultaneous aeration, 10 to 60% of monochlorophenols, dichlorophenols and trichlorophenols after one hour of treatment [25].

Combinations of ozonation, ultra-violet irradiation and powdered activated carbon (PAC) were used to treat acid, caustic and combined bleach plant effluents [26]. Use of PAC removed 30.2 to 43.7%, 18.7 to 78.7% and 13.2 to 53.0% of low MW TOX in acid, caustic and combined effluent streams. The removal efficiency fluctuated with the choice of PAC used. Removal efficiencies for total TOX were 82 to 86%, 47 to 48% and 73 to 74% respectively. On combined mill effluent the addition of ozone and ultra-violet oxidation produced removal efficiencies of 83% for the <1000 MW fraction of TOX and up to 14% for the <500 MW fraction. The addition of ozone to PAC in itself produced no improvement in removal efficiency.

Oxidation of alkali stage effluents with oxygen has been shown to remove 70 to 80% of the total organochlorine load in a mass transfer controlled process [14]. Total reaction time was approximately one hour with pressure and temperature not significant controlling parameters.

While reported removal efficiencies for oxidation-based treatment processes are promising, the cost of implementation at full scale is prohibitive [6].

Alkali treatment: Treatment of chlorination stage effluents with caustic achieved AOX reductions of 37 to 54%. In bench scale tests the pH of the effluent sample was elevated to 10.5 and decreased to a pH of 9.0 to 9.7 by the end of the reaction [27]. Combination of the alkali treatment with ultra violet (UV) irradiation increased AOX removal to 92%. The effluent samples were irradiated at a pH of 1.7 then alkali treated in a similar manner. A separate experiment combined alkali treatment with a fixed bed aerobic reactor as a post alkali treatment step. The treatment combination reduced AOX by greater than 70%.

Electrolytic treatment: Bench scale electrolytic units have been tested on bleached kraft mill total effluents [28,29]. AOX removal efficiencies are in excess of 99%. The process employs electrodes of varying composition and various hydraulic residence times to achieve the reported treatment efficiency. However, the high removal efficiencies may be offset by prohibitive energy costs.

Non-traditional biological degradation:

TABLE I. REPORTED ASB REMOVAL EFFICIENCIES FOR CHLOROPHENOLS.

Compound group	Reduction range [%][a]
Dichlorophenols	22-63
Trichlorophenols	-11-57
Tetrachlorophenols	22-67
Pentachlorophenols	25
Dichloroguaiacols	0-89
Trichloroguaiacols	-400-81
Tetrachloroguaiacols	80
Dichlorocatechols	-115-45
Trichlorocatechols	-30-41
Tetrachlorocatechols	13-57
Monochlorovanillins	92-100
Dichlorovanillins	81-96

[a] Source: 10, 40, 42, 45, 46.

White rot fungi are the only microorganisms known to degrade polymeric lignin and in particular chlorinated lignin of pulp mill origin [6,10]. They have been reported to degrade both low and high molecular weight chlorolignins effectively [10] but require a carbon energy source to produce hydrogen peroxide which in turn degrades the lignin.

Numerous authors have studied the ability of the white rot organisms to decrease the concentration of AOX and chlorinated organics from pulp mill effluents [24,30,31,32,33,34,35]. The "MyCoR" process, which uses the white rot fungi (*Phanerochaete chrysosporium*) within a rotating biological contactor, has been granted a U.S. patent and has been tested at bench scale. Removal of AOX has been reported at 70% with a two-day retention period [6,10]. A TOCl removal efficiency of 50% in a bench scale biological contactor, using *Phanerochaete chrysosporium*, over one day of treatment has also been reported [31].

Optimization of the MyCoR process produced removal efficiencies of 49% for extraction-stage high-MW TOCl in one day, and 62% in two days. Low-MW TOCl was reduced by 62% in one day. TOCl removal for the whole effluent was reported as 45% [30]. Further optimization resulted in a 50% AOX reduction in six hours for whole effluent.

Individual chlorovanillins, chlorophenols and chloroguaiacol in a bleached kraft effluent were also reduced to trace concentrations through the MyCoR process [35]. Another strain of white rot fungi (*Sporotrichum pulverulentum*) was reported to degrade 35 to 45% of low MW chlorolignins from spent bleach plant liquors [33]. In a test using other white rot fungi, *Trametes versicolor* was reported to reduce AOX from a bleach plant effluent by 25% in 24 hours [32].

White rot fungi have not been used in industry because of the economic limitations of satisfying the large energy requirements that degradation of spent bleach plant liquors require [10]. A further drawback is the reported generation of chlorinated veratrole compounds during degradation by white rot fungi [24]. The chlorinated veratroles are more lipophilic than the nonmethylated chlorolignins and hence are more likely to bioaccumulate in aquatic organisms.

Aerated stabilization basin: Aerated stabilization basins (ASBs) are the most common method of treating pulp mill effluents, largely because of their ability to remove BOD_5. However, they are not traditionally an efficient system for removal of AOX/TOCl. Various authors have reported AOX removal efficiencies across aerated lagoons ranging from 16 to 68% [7,36,37,38,39,40,41,42]. Little seasonal variation in AOX/TOX removal has been observed [37,39], except for low-MW AOX [7].

Experiments on recirculation of biomass in aerated lagoons have indicated that a four-fold increase in lagoon biomass could increase removal efficiency from 50 to 60% [10]. Significant work has been done to determine the mechanism of AOX removal in aerated lagoons [7, 38, 39, 40, 43, 44]. It has been postulated that AOX removal occurs by biosorption of organohalides to biomass and anaerobic dehalogenation and degradation in the benthal layer of the lagoon with biosorption providing the transport mechanism [39,40, 43,44]. Both high and low MW chlorolignins are reported to adsorb to aerobic biomass but aerobic dehalogenation was not reported [40].

Conversely, it has been suggested that the majority of AOX removal in an aerated lagoon is due to aeration enhanced hydrolytic splitting of chlorine from the organic substrate [38]. It is said that the mixed liquor suspended solids (MLSS) levels in an aerated lagoon are too small to allow significant biosorption to sludge.

Analysis of relative removals of different MW fractions in three North American ASBs was reported [7]. Low MW AOX was removed more effectively (43 to 63%) than high MW AOX (4 to 31%). Effluent AOX removal from mills using hardwood and softwood furnishes was comparable but furnish changeovers reduced the removal performance. In a separate, lab scale ASB study, degradation of hardwood derived TOCl was greater (44 to 52%) than for softwood derived TOCl (44%) [38].

Reduction of individual chlorinated organics across aerated basins has been reported by various authors [10,40,42, 45,46]. Individual removal efficiencies for various chlorophenols, provided in Table I, range from 30 to 89%. Information obtained from Paprican has indicated removal efficiencies up to 100% for chlorinated vanillins.

Activated sludge: Activated sludge and ASBs are the most common mill-scale effluent treatment systems. Activated sludge systems are reported to remove much higher quantities of AOX than aerated lagoons [6,10]. Removal efficiencies ranging from 14 to 65% have been reported [7,42,47,48,49,50,51,52,53,54,55].

Removal efficiencies for individual chlorinated organics range from 18 to 100% [42,47,49,56, 57] and are presented in Table II. AOX removal efficiency was correlated to sludge retention time (SRT) and to hydraulic retention time (HRT) [49] in pilot-scale tests of air and oxygen activated sludge systems. The maximum reported AOX removal efficiencies (> 40%) were achieved for SRTs greater than 20 days and HRTs greater than 15 hours. No significant difference in performance was observed between air and oxygen activated sludge systems. Further, the results supported the theory of aerobic dehalogenation as very little organochlorine was adsorbed to the biomass.

In a separate report on Finnish activated sludge systems, the highest AOX removals (45%) in mill scale units were reported for SRTs greater than 50 days [51].

Aerobic/anaerobic: Aerobic/anaerobic processes have been developed under the name of the Enso-Fenox process [58] and have been applied in two full-scale plants in Finland for treatment of bleach plant effluents. AOX removal efficiencies of 20 to 30% and chlorinated organics removal efficiencies of 64 to 94% have been reported over a hydraulic retention time of only seven hours [10,11].

AOX removal efficiencies up to 68% have been reported for laboratory scale systems with an HRT of 24 hours and SRT of >100 days. Removal efficiencies of 35 to 62% were reported for a pilot scale unit treating total bleach plant effluent with an HRT of 48 hours [51]. In separate studies of sequential anaerobic/aerobic treatment, AOX reductions of 28 to 47% for sulphite and 52 to 64% for kraft effluents were reported for the low-MW organochlorine fraction with reductions up to 95% for individual chlorinated phenolics [17,59,60,61].

Complete dechlorination of monochlorophenols and dichlorophenols was reported [60] in one study and 52 to 95% removal of chlorophenols was reported in another [58]. However, at present the technical feasibility of a full-scale industrial facility remains to be determined [62].

Summary of external treatment system

TABLE II. REPORTED ACTIVATED SLUDGE REMOVAL EFFICIENCIES FOR CHLOROPHENOLS.

Compound group	Reduction range [%][a]
Dichlorophenols	78
Trichlorophenols	51-69
Tetrachlorophenols	86-100
Pentachlorophenols	50-80
Dichloroguaiacols	67-97
Trichloroguaiacols	18-97
Tetrachloroguaiacols	59-99
Dichlorocatechols	37
Trichlorocatechols	63-95
Tetrachlorocatechols	59-90
Monochlorovanillins	94
Dichlorovanillins	100

[a] Source: 42, 47, 49, 56, 57.

performance for AOX removal: Figure 2 illustrates the reported ranges of AOX removal efficiencies, for both pilot- and full-scale units, for the various individual treatment systems reviewed. The highest removal efficiencies were reported for chemical precipitation, ultrafiltration, UV irradiation and reverse osmosis. However, high removal efficiencies were achieved when these methods were applied selectively, either to chlorination, or to extraction stage effluents and do not reflect treatment of whole mill effluent.

Figure 3 presents treatment ranges for combinations of various treatments systems which may be applied to whole mill effluent through pretreatment of concentrated bleach plant streams and secondary treatment of the remaining effluent. Highest removal efficiencies were achieved for the combination of ultrafiltration and anaerobic/aerobic systems, ultraviolet and alkali treatment (chlorination stage effluent only) and ultrafiltration and reverse osmosis treatment (extraction stage effluent only).

Figure 4 illustrates removal efficiencies for chlorinated phenolics as reported for various treatment systems. Highest removal efficiencies were reported for anaerobic/aerobic, activated sludge and ion exchange systems.

Figure 5 compares chlorinated phenolic and AOX removal efficiencies for various treatment systems. Removal of chlorophenols is consistently greater than removal of AOX. Hence, the more toxic (and lower MW) compounds are being preferentially removed relative to the bulk organochlorine group measured as AOX.

It is important to note that the comparison of treatment efficiencies presented herein does not consider capital and operating costs, or land requirements, but simply the technical feasibility of chlorinated organics removal.

AOX AS REGULATOR

The preceding section has reviewed various external treatment methods for removing AOX and detailed some of the factors affecting performance. However, the discrepancy between removal of the bulk organochlorine feature, AOX, and the removal of more toxic, lower MW, chlorinated phenolics observed across a wide range of treatment systems brings into question the value of a non-specific measure such as AOX (or TOX or TOCl) as a regulatory parameter.

Several authors have cited the difficulties that arise when using AOX as such a tool [63,64,65,66,67]. The variable concentration of individual chlorinated organics within the AOX group and, in particular, the highly toxic chlorinated phenolics, implies that AOX, in

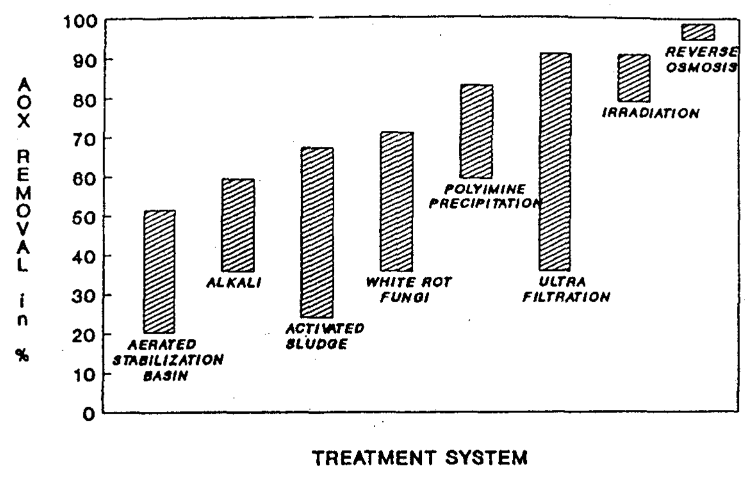


FIG. 2. REPORTED RANGE OF AOX REMOVAL FOR VARIOUS EXTERNAL TREATMENT SYSTEMS.

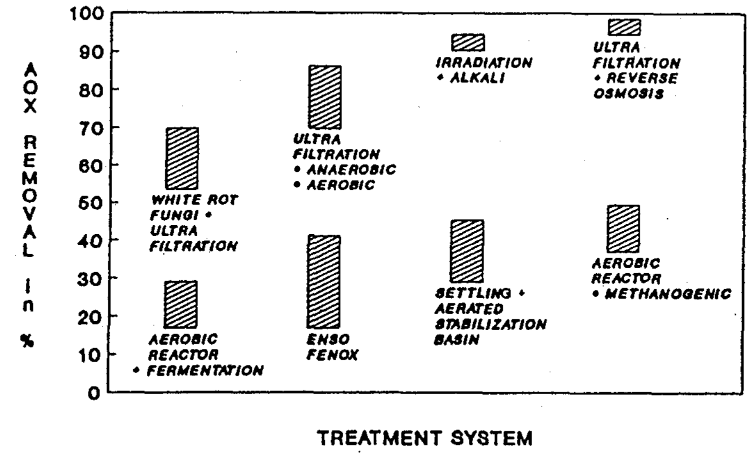


FIG. 3. REPORTED RANGE OF AOX REMOVAL FOR VARIOUS COMBINATIONS OF EXTERNAL EFFLUENT TREATMENT SYSTEMS.

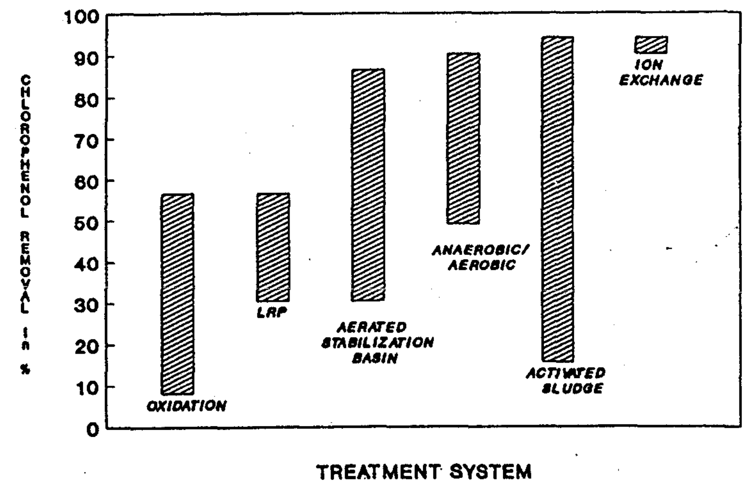


FIG. 4. REPORTED RANGE OF CHLOROPHENOL REMOVAL FOR VARIOUS EXTERNAL TREATMENT SYSTEMS.

itself, is not a dependable indication of effluent toxicity. Further, assessment of the contribution of individual compounds to total toxicity indicates that resin and fatty acids may also contribute a substantial fraction of the total toxicity of a pulp mill effluent [65]. By definition, these compounds are not even considered in the AOX test.

Recent lab scale bleaching trials indicate a disproportionate reduction in toxicity compared to AOX for certain process modifications [65]. This indicates that reduction in AOX, through process modifications or treatment, does not provide a true indication of the concomitant, and greater, reduction in effluent toxicity. Figure 5 illustrates paired removal efficiencies for chlorophenols and AOX for different treatment systems. The highly toxic chlorophenolic portion of the bleached mill effluent is consistently, and preferentially, removed over the total AOX or TOCl. This effect is particularly pronounced for activated sludge [49] or aerobic/anaerobic [17,58] systems.

Further, the concept of assessing toxicity equivalence to individual components of the AOX and measuring total effluent toxicity relative to the most toxic component has been discussed by several authors [63,64,65,68]. If the toxicity equivalence factors suggested in Holloran et al. [65] are applied to literature removal efficiencies from an activated sludge plant [56], it may be seen in Fig. 6 that the toxicity due to chlorophenols is reduced by 50%. The toxicity of the resin and fatty acids (RFA) is reduced over 90% and the total toxicity equivalence of the effluent is reduced by over 90%.

While the authors [56] did not report AOX removal efficiencies, the previously reviewed literature suggests that it would likely have been in the range of 40 to 60%. A similar calculation was made for chlorophenol removal efficiency in two ASBs [46], Fig. 6. Here, for AOX removals of 23 and 30% the corresponding decrease in toxicity equivalence due to the chlorophenols (resin and fatty acids not reported) were 31 and 37%. Hence, it is evident that removal of AOX on its own underestimates the reduction in toxicity, or biological effect of the effluent. Consequently, the focus of studies on optimization of existing or development of new treatment systems should be placed on the reduction of the toxicity of the effluent and of the toxic constituents within AOX rather than the reduction of AOX itself.

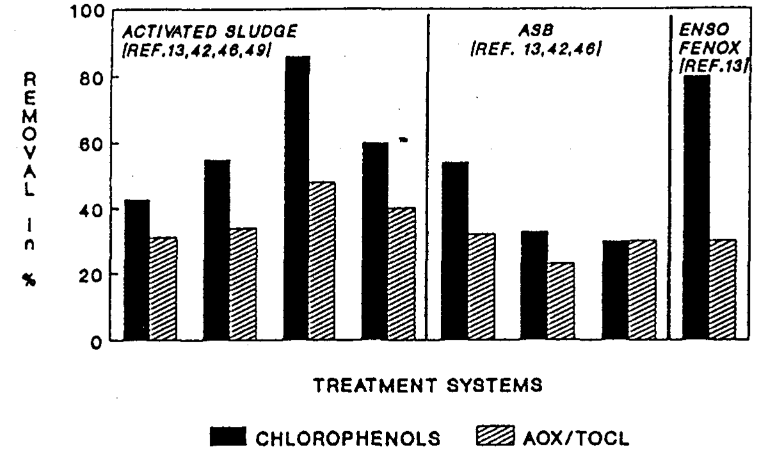


FIG. 5. TREATMENT OF BLEACHED PULP MILL EFFLUENT, CHLOROPHENOL VS. AOX REMOVAL.

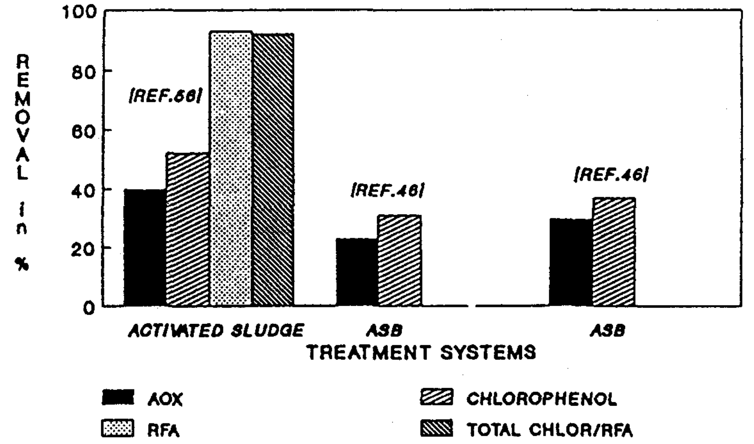


FIG. 6. TREATMENT OF BLEACHED PULP MILL EFFLUENT, TOXICITY EQUIVALENCE REMOVAL.

CONCLUSIONS

A review of the existing literature on the removal of AOX and chlorophenols in external treatment systems has been done. Although bench- and pilot-scale trials of various systems have produced high reductions in AOX/TOCl and chlorophenols, their feasibility has not been demonstrated in mill scale application. Consequently, best available technology economically achievable (BATEA) is still conventional biological treatment, which provides a more limited AOX removal, typically less than 50%.

However, removal efficiencies for the lower MW, toxic, compounds within the AOX group are substantially greater.

The implications for the pulp and paper industry of the proposed federal effluent discharge guidelines are far reaching. If bleached kraft pulp mills are regulated to AOX discharge guidelines of 1.5 kg/adt, the application of BATEA in secondary treatment, with AOX removal efficiencies in the 40 to 60% range, will necessitate AOX discharges of less than 3.0 kg/adt in the untreated effluent.

The process modifications required to achieve this AOX discharge level include combinations of MCC digesters, oxygen delignification, high chlorine dioxide substitution ratios in the first bleaching stage, and oxygen and peroxide enhanced extraction. The cost to implement this technology in all Canadian mills has been estimated at one billion dollars [64].

With such an extreme cost it is prudent to view the goal of regulating effluent AOX discharge, the protection of the aquatic environment. Hence, the reduction of both acute and chronic toxicity in pulp mill effluents is of concern. Several authors have concluded, or provided data to illustrate, a poor correlation between acute or chronic toxicity and AOX [5,42,67,69]. Moreover, approximately 80% of the AOX in bleach plant filtrate is high MW material that is unlikely to be biologically active.

Experimental exposure studies have indicated no effect on fish growth or reproduction when exposed to AOX levels far greater than those present downstream of the majority of pulp mills [67].

Regulation of AOX to 1.5 kg/adt or any other arbitrary level is of little value unless justified on a sound technical basis. A regulation based on the more meaningful compounds within the biologically active portion of the AOX is required. Future development work on effluent treatment systems should focus on the removal of the toxic constituents of AOX rather AOX itself.

Effluent regulations based on individual compounds of known toxicity and bioaccumulation potential or based on toxicity weighted sums of individual compounds, are suggested by several authors [63,64,65,67,68]. These would achieve the desired goals of controlling the effect and toxicity of pulp and paper effluent discharges, focussing future treatment system optimization and avoiding the enforcement of a large and unjustified economic burden on the pulp and paper industry.

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Résumé: Cette communication passe en revue divers systèmes de traitement externe d'effluents de pâtes et papiers pour l'enlèvement des COA (composés organiques absorbables) et des produits organiques chlorés individuels. Les concentrations en produits organiques chlorés individuels des effluents traités sont pondérées selon leur toxicité équivalente. De plus, l'efficacité de chaque traitement en fait de réduction de la toxicité équivalente est comparée à celle de la réduction des COA. La communication poursuit avec la recommandation d'une ligne directrice à suivre en ce qui concerne l'évacuation des effluents de pâtes et papiers, basée sur les mesures pondérées de toxicité des organochlorés plutôt que sur celles des COA/CLOT.

Abstract: A review of various external pulp and paper effluent treatment systems for removal of AOX and individual chlorinated organics is provided. Treated effluent concentrations of individual chlorinated organics are weighted for their equivalent toxicity. Equivalent toxicity removal efficiencies are compared to that of AOX. The development of pulp and paper effluent discharge guidelines based on toxicity weighted measures of organochlorine rather than AOX/TOCl is recommended.

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