

Removal of chlorophenolics from an aerated lagoon

John Graves, Hasan Jameel, and Thomas W. Joyce

ABSTRACT: *The effects of aerobic treatment, chlorine dioxide substitution, and oxygen delignification on specific chlorinated organic compounds found in softwood pulp bleaching effluents were studied. The compounds of interest were chlorinated phenols, catechols, guaiacols, vanillins, and syringols, although vanillins and syringols were not detected in this study. All three methods were effective in reducing initial AOX and toxicity. All of the compounds examined responded favorably to aerobic biological treatment, with individual removal efficiencies varying from 29% to 100%. Increasing chlorine dioxide substitution decreased the concentration of polychlorinated phenolic compounds in the combined bleaching effluent. Response to oxygen delignification was not as clear. In general, the quantity of chlorinated compounds detected before biological treatment decreased with increasing substitution and oxygen delignification. After biological treatment, there were minor differences between a sequence with 100% ClO_2 substitution and a sequence using oxygen delignification. Therefore, O_2 delignification does not present a real benefit if 100% ClO_2 bleaching is practiced.*

KEYWORDS: *Adsorbable organic halogen, aerobic process, biological treatment, bleaching effluents, chlorine compounds, chlorine dioxide, delignification, effluent treatment, lagoons, oxygen bleaching, phenols, softwood pulps.*

As many mills have reduced the amount of BOD and suspended solids entering their wastewater treatment facilities, other pollutants have become of greater concern. Mills using chlorine-based com-

pounds for bleaching discharge chlorinated organics into the environment. Although a matter of controversy, some of these compounds may be toxic and mutagenic (1,2,) and may bioaccumulate in fish tissue (3). 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 use of oxygen delignification or substitution of chlorine dioxide for chlorine. These techniques serve to reduce chlorinated organics as well as BOD, COD, and toxicity (1, 4–6).

AOX is a sum parameter that is used to gauge the chlorinated content of waste waters. This parameter is important because only about 5% of the organically bound chlorine in paper mill waste waters has been identified as specific compounds (7). Approximately 300 compounds have been isolated in C- and E-stage effluents. Among these compounds are a family of structurally related compounds, including chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols, and chlorovanillins. A comparison with TOCl (total organic chloride) content indicated that about 10% of the low-molecular-weight (LMW) compounds in C-stage effluent were identified. The same comparison for E-stage effluent accounted for 35% of the low-molecular-weight compounds (8). These LMW compounds, comprised of chlorinated phenols, guaiacols, and catechols, account for 47% of the

Graves, Jameel, and Joyce are, respectively, graduate student, professor, professor, Department of Wood and Paper Science, North Carolina State University, Raleigh, NC 27695.

Effluent Treatment

I. Pollutants selected for study

Trichlorosyringol	TCS
4,5,6-trichloroguaiacol	4,5,6-TCG
3,4,5-trichloroguaiacol	3,4,5-TCG
3,4,5-trichlorocatechol	3,4,5-TCC
2,4,6-trichlorophenol	2,4,6-TCP
Pentachlorophenol	PCP
Tetrachlorocatechol	TeCC
Tetrachloroguaiacol	TeCG
2,4,6-trichloroguaiacol	2,4,6-TCG
5-chlorovanillin	5-CV
4-chlorocatechol	4-CC
4,5-dichlorocatechol	4,5-DCC
4-chloroguaiacol	4-CG
4,5-dichloroguaiacol	4,5-DCG
4,6-dichloroguaiacol	4,6-DCG

II. Chlorinated organic compounds removed by aerated lagoon treatment. (D+C)E₀DED bleaching of pine (9).

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

LMW chlorinated material produced per ton of kraft pulp (9).

The new proposed EPA Cluster Rule will not permit the discharge of substituted (chlorinated) phenols at detectable levels. Of particular concern are several specific chlorinated phenolics (**Table I**) since they have been previously identified in bleach plant effluents. The objective of this study was to analyze the effectiveness of laboratory-scale aerated lagoons to remove chlorinated phenols.

III. Bleaching conditions for softwood pulp

	Oxygen	C-stage	E ₀ -stage
Consistency, %	20	3.5	12
Temp., °C	105	40	75
Time, min	30 to temp 30 at temp	60	20 with pressure 40 without pressure
Charge, %	1.9	0.22 x Kappa	0.625 x Available Cl
Pressure, psig	100	Atmospheric	30
Notes:	45% delignification	0, 50, or 100% ClO ₂ substitution	

Reduction of chlorophenolics by process modifications

Process modifications, such as oxygen delignification and chlorine dioxide substitution, can reduce the amount of AOX produced by 45% and 70%, respectively (6). Additionally, the quantity and the type of chlorophenolics produced are affected. When oxygen delignification and ClO₂ substitution (30%) are employed, the total amount of chlorinated phenolics produced is reduced approximately 20%. Also, the presence of tetrachlorinated compounds are no longer detected. As the substitution level is increased further, the chlorinated phenolic level continues to decrease (10).

Removal of chlorinated compounds by aerated lagoons

Overall removal of AOX in an aerated lagoon system varies from 15% to 50% of the total AOX (6, 11–13). But higher AOX removal is observed for low-molecular-weight (LMW; < 1 kD) chlorinated compounds as compared to the total AOX. Removals of 43–60% of LMW AOX have been reported (12, 14). This increase in removal efficiency may be due to the transport of LMW compounds through bacterial cell membranes and the resulting biodegradation. Bryant and Amy (7) have found a positive correlation between the presence of LMW chlorinated organics and both acute and chronic toxic-

ity. Gergov *et al.* (9) did not observe a correlation between *Daphnia* toxicity tests and total AOX. Only about a 20% reduction for high-molecular-weight AOX (HMW; > 1 kD) has been observed (14). The reduction in some specific chlorinated organics is presented in **Table II**. The specific mechanisms which effect the removal of chlorinated organics have not been determined (15).

As seen in Table II, the chemical structure affects the amenability to biological treatment. For example, chlorocatechols are more easily degraded than are chloroguaiacols (9). Compounds with a chlorine atom in position six have shown particular resistance to microbial degradation (16). In general, as the degree of

IV. AOX impact summary for all process modifications (mg/L)

	<i>CEo</i>	<i>(D/C)Eo</i>	<i>DEo</i>	<i>OCEo</i>	<i>O(D/C)Eo</i>	<i>ODEo</i>
Total						
Before ^a	142	98	65	106	75	55
After ^a	122	84	37	73	53	37
MW < 1000 D						
Before ^a	89	66	56	82	53	48
After ^a	68	45	36	45	41	26

^aBefore or after aerobic biological treatment

chlorination, i.e., the number of chlorine atoms per molecule of chlorinated compounds, increases, so does their toxicity and bioaccumulation potential (17).

Experimental

Pulp

Bleachable grade softwood pulp was obtained from a mill in the south-eastern United States. Pulp was obtained before and after oxygen delignification with an average kappa number of 26 and 14, respectively. Pulp bleaching conditions are presented in **Table III**.

Biological treatment

Simulated bleach plant effluents were treated in bench-scale aerated lagoons with a 6-day hydraulic detention time. Effluents were composed of chlorination and oxidative extraction stage filtrates in a 3:1 ratio. It was decided not to include the D-stage filtrate because standard washing procedures preclude its immediate combination with other filtrates. Oxygen delignification filtrate was also not included since all of this effluent is sent to the recovery system. Additionally, the first chlorination and extraction stages account

for approximately 85% of the total BOD and color of bleach plant effluents (18).

Nutrients were added in the ratio of BOD:N:P::100:5:1 (19). Nitrogen was added as ammonium sulfate and phosphorus was added as potassium phosphate monobasic. The pH of the effluent was adjusted to between 6.9 and 7.1, and the effluent was stored in a 50-L polyethylene bottle at 4°C.

The simulated aerated lagoons consisted of two 3-L Plexiglas reactors connected in series. The reactor volume was moderately agitated and aerated with compressed, scrubbed air to ensure an adequate level of dissolved oxygen in the reactors. The reactor volume was adjusted with an outlet weir which led to a 1-L separatory funnel for sample collection. A peristaltic pump supplied effluent to the reactors at a rate of 1 L per day. The inlet reservoir was filled daily with 1 L of effluent which had been allowed to equilibrate to room temperature. At startup, a seed microorganism was added to obtain 500 mg/L total suspended solids (TSS) in the reactor. Antifoam B (Sigma Chemicals) was added as needed to control foam generation, and the solids that accumulated above the waterline were returned daily to the mixed liquor.

Reactor effluents were tested daily for COD, TSS, pH, and temperature to evaluate performance. Steady state was assumed when the COD of the system remained essentially constant, i.e., the 5-day running average did not vary by more than 10%. The system was allowed to run for an additional 7 or 8 days, during which time the effluents were collected for analysis. Effluent samples were stored in acid-rinsed, amber glass bottles at 4°C.

Toxicity

Toxicity was measured with the Microtox Model 500 basic test protocol (Microtox Operation Manual). The effect of a test solution, in this case effluent, on bioluminescent bacteria, is determined by measuring the decrease in light output. The results are reported as an EC_{50} value. EC_{50} is the concentration of effluent at which the emitted light is decreased by 50% after a specified period of time, 5 or 15 min. A high EC_{50} indicates low toxicity. The Microtox test has been correlated with fish toxicity (20, 21).

Ultrafiltration

Ultrafiltration was performed in an Amicon Model 8400 ultrafiltration unit with an operating pressure of 55 psig. Amicon YM2, MW > 1000, membranes were used for fractionation of effluents.

Chlorophenol extraction

To a 25-mL effluent sample, 0.75 mL of 2,6-dibromophenol solution in ethyl acetate (0.268 µg/mL, internal standard) was added, followed by 25 mL of 0.1 mol/L K_2CO_3 solution and 1 mL acetic anhydride. The mixture was vigorously shaken for 1 min, after which the chlorophenols were extracted twice with 5 mL portions of methylene chloride. The solvent layer was separated and dried over Na_2SO_4 . This method was modified from that of Lindstrom and Mohamed (22).

Effluent Treatment

V. Toxicity of bleach plant effluents before and after biological treatment ($EC_{(50)}^{-1}$)

	Influent	Effluent
CEo	0.06	0.03
(D50 + C50)Eo	0.05	0.02
DEo	0.04	0.01
OCEo	0.04	0.02
O(D50 + C50)Eo	0.04	0.02
ODEo	0.03	0.01

VI. Chlorophenols in pulp bleaching effluents before biological treatment, $\mu\text{g/L}$

Compound	Sequence					
	CEo	C/DEo	DEo	OCEo	OC/DEo	ODEo
<i>Phenols</i>						
2,4,6-TCP	0.09			0.04		
PCP	0.04					
<i>Catechols</i>						
4-CC	8.83					
4,5-DCC	3.13	1.35				
TeCC	0.46	0.3		0.533	0.39	
<i>Guaiacols</i>						
4-CG	254	211	191	89.6	68.8	59.3
4,5-DCG	160.3	157	116	542	311	275
4,6-DCG	2.35	0.57	0.50	1.45		
3,4,5-TCG	0.13	0.08		0.12	0.12	
4,5,6-TCG	0.27	0.09		0.28	0.10	

GC analysis

Gas chromatography was performed on a Hewlett-Packard 5890A system equipped with an automatic sampler and an ECD detector. An open tubular column (30 m x 0.31 mm ID, DB-5 phase with film thickness of 0.25 μm ; J&W Scientific) was used. Helium was used as the carrier gas with a flow rate of 2.5 mL/min and nitrogen as the makeup gas (55 mL/min). The injector was set in the splitless mode. The oven temperature profile was 1 min hold at 45°C, from 45°C to 120°C at 15°C/min, from 120°C to 230°C at 2°C/min, 5 min hold at 230°C, and the final temperature was 250°C. Injector temperature was maintained at 200°C and detector temperature was maintained at 280°C.

Results and discussion

AOX

The quantity of AOX detected in each sequence is reported in **Table IV**. The measure of AOX is a very general test which combines the presence of all halogenated compounds. The formation of low-molecular-weight AOX compounds is of concern because of their ability to enter biological organisms. As shown

by the data in Table IV, non-oxygenated sequences, in general, form a slightly higher fraction of compounds under 1000 Daltons than sequences involving oxygen delignification. Even though the removal of these low-molecular-weight compounds is slightly higher in the oxygen delignified sequences (37% versus 30%), the result after biological treatment was similar to the conventional sequences.

The data in Table IV demonstrate that the removal of total AOX by biological treatment for the non-oxygenated sequences is less than that for the oxygenated sequences. This is due to the higher initial toxicity of the sample to aquatic microorganisms. However, the final AOX after biological treatment was equivalent in the oxygenated sequence with 100% ClO_2 and the conventional 100% ClO_2 sequence.

ClO_2 substitution was effective in reducing the quantity of AOX formed. Increasing the ClO_2 substitution level from 0% to 100% reduced AOX by 50%. Oxygen delignification reduced the formation of total chlorinated compounds by 24% before biological treatment. However, the final comparison after biological treatment shows little difference between the conventional and the oxygen delignified sequences. Biological

treatment was also effective in reducing AOX.

Toxicity

Toxicity is primarily due to low-molecular-weight compounds which can penetrate into the organism. Biological treatment removed 59% of the apparent toxicity as measured by the Microtox method (**Table V**). A smaller percentage of the toxicity is removed in the oxygenated sequence, but this is due to the lower initial levels. ClO_2 substitution decreased toxicity by 30% and oxygen delignification decreased toxicity 26%. Additionally, the no- ClO_2 substitution sequence with oxygen delignification has the same toxicity as a sequence with 100% ClO_2 substitution and no oxygen delignification. The final toxicity after biological treatment is the same for both the conventional and nonconventional bleaching sequences.

Phenols

The presence of chlorinated phenols (**Tables VI and VII**) was found only in the sample with no- ClO_2 substitution, with the formation of 55% more 2,4,6-TCP (trichlorophenol) than PCP (pentachlorophenol). At ClO_2 substitution levels of 50% and

VII. Chlorophenols in pulp bleaching effluents after biological treatment, µg/L

Compound	Sequence					
	CEo	C/DEo	DEo	OCEo	OC/DEo	ODEo
<i>Phenols</i>						
2,4,6-TCP						
PCP						
<i>Catechols</i>						
4-CC						
4,5-DCC						
TeCC	0.03					
<i>Guaiacols</i>						
4-CG	78.8	57.6		2.0		
4,5-DCG	140	131	91	199	182	225
4,6-DCG	1.39	0.53		0.84		
3,4,5-TCG						
4,5,6-TCG	0.11	0.06		0.04		

greater, the formation of chlorinated phenols was not detectable. Oxygen delignification decreased the formation of 2,4,6-TCP by 52% in the no-ClO₂ substitution sequence. PCP was not detectable in effluents with oxygen delignification. After effluents were treated biologically, chlorinated phenols were no longer detectable. Thus, the inclusion of oxygen delignification, increases in ClO₂ substitution levels, and biological treatment are effective in the reduction of these chlorinated phenolics. Oxygen delignification, however, was not needed as a method for chlorophenolic reduction because biological treatment was completely effective in removing chlorophenolics.

Guaiacols

The most predominant of the compounds examined were the chlorinated guaiacols. More 4,5-DCG (dichloroguaiacol) was formed than 4,6-DCG due to the higher reactivity of the C-5 site. The formation of guaiacols with three and four chlorine moieties was even less than that of the monosubstituted compounds. Tetrasubstituted guaiacols were not detected in these effluents.

4-CG decreased 25% in sequences without oxygen delignification as

ClO₂ substitution increased. Sequences involving oxygen delignification resulted in a 34% decrease in formation of 4-CG. Biological treatment reduced the amount of 4-CG by an overall 90%, with a higher percentage of the compound being removed in sequences involving oxygen delignification. This observation corresponds with a lower initial effluent toxicity level in the oxygen delignified pulps.

4,5-DCG was reduced by 38% with increases in ClO₂ substitution. Biological treatment reduced 4,5-DCG by an overall 29%. A higher quantity of the compound was detected in the oxygen delignified sequence. Therefore, oxygen delignification is not an effective means to reduce the formation of 3,5-DCG. Biological treatment reduced 4,5-DCG by 41% in sequences involving oxygen delignification as compared to a 17% reduction in sequences not utilizing oxygen. Even after biological treatment, the quantity of 4,5-DCG in the conventional sequences was less than the oxygen delignified sequences.

4,6-DCG was found in significantly smaller quantities than 4,5-DCG. Increasing ClO₂ substitution from 0 to 100% and oxygen delignification reduced 4,6-DCG by 89% and 69%, respectively. Biological treatment of

the bleaching effluents removed 47% of 4,6-DCG.

3,4,5-TCG formation was low compared to other chlorinated guaiacols. Its formation was completely reduced by increasing chlorine dioxide substitution, but was not reduced by oxygen delignification. Thus, oxygen delignification did not seem to be effective in reducing the formation of 3,4,5-TCG. In all cases where 3,4,5-TCG was detected, biological treatment completely removed the compound.

4,5,6-TCG formation was reduced by 100% by increasing the chlorine dioxide substitution level from 0 to 100%. Biological treatment reduced pollutant levels by 72%. The use of oxygen delignification was ineffective in the removal of 4,5,6-TCG. The values were very similar in both the oxygen delignification and conventional sequences at the same chlorine dioxide substitution levels.

Catechols

4-CC was completely eliminated by increasing the ClO₂ substitution level from 0 to 100% in non-oxygen delignified effluents. 4-CC was not detected in oxygen delignified pulp effluents. Biological treatment completely eliminated the quantity of 4-CC detected. The quantity of 4-CC found in effluents was reduced effectively by all treatments.

4,5-DCC was present in similar quantities to 4,6-DCG. Removal efficiency by oxygen delignification, increasing chlorine dioxide, and biological treatment was 100% in cases.

The formation of TeCC (tetrachlorocatechol) was reduced 98% by biological treatment and 100% by increasing the chlorine dioxide substitution. However, the inclusion of oxygen delignification appeared to increase the quantity of TeCC by 20%. Tsai *et al.* (23) suggest that oxidative demethoxylation during oxygen delignification leaves catechol moieties in residual lignin, and these structures are particularly susceptible to chlorination.

Effluent Treatment

The presence of catechols in this study was limited to 4-CC (4-chlorocatechol), 4,5-DCC (4,5-dichlorocatechol), and TeCC. Since other studies (23) have found other chlorinated catechols in similar effluents, other extraction methods could yield different results. All treatment methods examined were completely effective in the removal of all chlorinated catechols. However, since 100% ClO_2 substitution and/or biological treatment removed all chlorinated catechols, oxygen delignification was not required.

General observations

Of the 15 chosen compounds, 10 were detected in the effluent samples. The five not detected were 5-CV, 3,4,5-TCC, TCS (trichlorosyringol), 3,4,6-TCG, and TeCG. Of these five, TCS was not expected since the pulp bleached was 100% softwood. A summary of the results of the detected chlorinated compounds are displayed in Tables VI and VII.

Summary and conclusions

Biological treatment was quite effective in decreasing the chlorinated compounds in the effluent. The decrease in overall AOX was 15-43%, while removal of the individual chlorinate species (phenols, catechols, and guaiacols) varied from 12% to 100%. In most instances, an aerated lagoon was very effective in decreasing the chlorinated pollutants selected in this study. The aerated lagoon had the greatest difficulty in removing 4,5-dichloroguaiacol. The

toxicity was also decreased by 50-75% across the aerated lagoon.

Process modifications such as chlorine dioxide substitution and oxygen delignification also decreased the AOX, toxicity, and selected chlorinated compounds. Using 100% chlorine dioxide substitution, the AOX could be decreased by 54% for the untreated effluent and 70% for the treated effluent. Only a 15% decrease in AOX was measured with oxygen delignification when it was used in the sequence with 100% chlorine dioxide. It is interesting to note that the AOX after effluent treatment was comparable for the D(EO) and OD(EO) sequences, especially after effluent treatment. The toxicities of the treated effluents for the D(EO) and OD(EO) sequences were comparable.

Both oxygen delignification and chlorine dioxide substitution decreased the chlorophenols studied. With 100% chlorine dioxide, only 4,5-dichloroguaiacol remained after biological treatment for the sequences with and without oxygen delignification. The sequence with oxygen delignification actually had a higher amount of 4,5-dichloroguaiacol in the treated effluent. Oxygen delignification did not show any benefits for AOX, toxicity, and the selected chlorophenols in the biologically treated effluents if 100% chlorine dioxide substitution was used. 

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Received for review July 7, 1994.

Accepted Jan. 6, 1995.