Effect of chlorine dioxide substitution, oxygen delignification, and biological treatment on bleach-plant effluent

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ABSTRACT: The study examines the effects of chlorine dioxide (ClO_2) substitution, oxygen delignification, and biological treatment on pollutant levels in simulated bleach-plant effluents. Biological treatment reduced COD, BOD, AOX, and toxicity but did not reduce color. ClO_2 substitution reduced discharge of all five pollutants, with a large reduction in AOX. Substitution did not influence the efficiency of pollutant removal by biological treatment. Oxygen delignification reduced discharge of the five pollutants, and effluents from sequences with oxygen delignification were easier to treat by aerobic methods.

KEYWORDS: Biological treatment, bleach plants, bleaching effluents, chlorine dioxide, delignification, oxygen, pollution, sequences, simulation, substitutes.

Recently, the effect of the pulp and paper industry on the environment has been closely examined. Mills that bleach pulp with chlorine-based compounds discharge chlorinated organics into the environment. Some of these compounds have exhibited toxicity and mutagenicity (*1, 2*) and may bioaccumulate in fish tissue (*3*). An increasingly attractive means to reduce the discharge of chlorinated organics, as measured by AOX (adsorbable organic halide) content, is to modify the bleaching process either by use of oxygen delignification or substitution of chlorine dioxide (ClO_2) for chlorine. These techniques serve to reduce chlorinated organics as well as BOD (biochemical oxygen demand), COD (chemical oxygen demand), and toxicity (*1, 4, 5*). Currently, AOX is not a regulated pollutant in the United States, but BOD, pH, and TSS (total suspended solids) are regulated (*6*).

BOD and acute toxicity are caused by biodegradable, low-molecular-weight compounds; high-molecular-weight compounds are the primary cause of COD, color, and chronic toxicity (*7*). The National Council for Air and Stream Improvement (NCASI) recently studied the effect of ClO_2 substitution on effluent BOD_5 (five-day BOD) and color. BOD decreased by 20–30% and color by 50–80% at 90–100% ClO_2 substitution (*8*). Other studies have shown that COD and color can be reduced by increasing ClO_2 substitution (*4, 5*).

ClO_2 substitution also reduces toxicity. A subcommittee of the CPPA Bleaching Technology and Development Committee stated that, with increased substitution, "the toxicity of chlorination and first-extraction-stage effluent is decreased, but the effect on the combined effluent from the entire sequence is smaller" (*9*). Pryke (*4*) and Singh (*5*) also reported that effluent toxicity decreases with increasing ClO_2 substitution.

The impact of AOX compounds on the environment will depend greatly on their molecular weight and C/Cl ratio (*10*). Low-molecular-weight (<1 kD)* compounds have a higher impact than those of high molecular weight (>1 kD), since they can penetrate the biological cell membrane (*11*). The major fraction of AOX in bleach-plant effluents consists of high-molecular-weight compounds (*12*). These compounds may biodegrade slowly to form chlorinated phenol, guaiacols, anisole, and veratroles (*2, 13*). The size of the compound also affects its susceptibility to biological

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*D represents the dalton, a unit of atomic mass.

treatment. Generally, the higher the molecular weight, the more resistant a compound is to biological degradation.

A low C/Cl ratio indicates a high degree of chlorine substitution, which generally increases the toxicity of the compound (*4*). Additionally, lipophilicity and bioaccumulation of chlorophenolic compounds increases with increasing chlorine substitution (*14*). The amount of chlorinated organic compounds formed is directly proportional to the consumption of elemental chlorine. As Cl_2 is replaced by ClO_2, the total elemental chlorine available decreases, and the quantity of chlorinated organics decreases (*4*). Annergren *et al.* (*15*) and Axegard (*16*) showed that at high levels of ClO_2 substitution, the formation of highly halogenated phenolic compounds decreases.

During aerobic treatment of whole-mill effluent from a bleached kraft mill, BOD decreases by at least 80% (*17*). Color is not affected by biological treatment, as it is caused by high-molecular-weight compounds that are resistant to biodegradation. Aerobic treatment reduces AOX by 25–60% (*18, 19*). Additionally, it has been found that 60% of the low-molecular-weight AOX compounds (<1 kD) are biodegraded as compared with 20% of the high-molecular-weight fraction (>1 kD) (*19*).

Oxygen delignification can reduce color by 70–90% (*17, 20*), BOD by 81%, and COD by 67% (*17*). The reduction is due to the recycle of the organic matter to the recovery boiler, where it undergoes combustion (*1*).

A variety of studies have provided information on the effect of process modification and biological treatment on the pollutant load in bleach-plant effluents, but the information is scattered through a variety of journals. One aim of the current study is to confirm the previous studies and tie the results together in one article. Another aim is to take the information a step further by examining the effect of process modifications on the efficiency of biological treatment.

I. Bleaching conditions for softwood pulp

	Oxygen	*C-stage*	*Eo-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, 100% ClO_2	

Experimental

Pulp

Bleachable-grade softwood pulp, with an average kappa no. 28, was obtained from a mill in North Carolina. Pulp bleaching conditions are listed in **Table I.**

Biological treatment

Simulated bleach-plant effluents were treated in bench-scale aerated lagoons with a six-day hydraulic retention 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 of standard washing procedures in mill operations, where the D-stage effluent is not immediately combined with other filtrates. Oxygen-delignification filtrate was 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 (*20*).

Nutrients were added in the ratio of BOD:N:P::100:5:1 (*21*). Nitrogen was added as ammonium sulfate and phosphorus was added as potassium phosphate monobasic. Effluent pH was adjusted to 6.9–7.1, 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 by 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 a 1-L sample of effluent that had been allowed to come to equilibrium with room temperature. Antifoam B (Sigma Chemicals) was added as needed to control foam generation, and the solids that accumulated above the water line were scraped into solution daily.

Seed microorganisms for the reactors were obtained from the underflow of the secondary clarifier of a bleached kraft mill in Virginia. The underflow contained 2.2% suspended solids; it was stored in a polyethylene container at 4°C until needed. At startup, 75 mL of sludge was added to each of the two vessels of the simulated lagoon to obtain approximately a 500-mg/L TSS in each vessel.

Reactor effluents were tested daily for COD, TSS, pH, and temperature to evaluate performance. Steady state was assumed to be achieved when the COD of the system remained essentially constant, i.e., the five-day running average did not vary by more than 10%. The system was allowed to run for an additional seven or eight 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

II. Effluent pollution loads from simulated bleach plant effluent before and after biological treatment

	COD, mg/L			BOD, mg/L			Toxicity, 1/[EC $_{50}$]			Color, Pt-Co units		
Source	In	Out	Removal, %	In	Out	Removal, %	In	Out	Removal, %	In	Out	Removal, %
C(EO)	1670	1220	27	300	30	90	0.04	0.03	16	6750	5130	24
(D50+C50)EO	1530	1100	28	220	30	86	0.03	0.02	40	3480	3480	0
D(EO)	1320	900	32	150	20	87	0.02	0.01	53	1960	1960	0
OCEo	1000	550	45	150	30	80	0.02	0.01	42	1600	1720	-8
O(D50+C50)EO	930	540	42	130	30	77	0.02	0.01	47	1250	1310	-5
OD(EO)	730	490	33	100	30	70	0.01	0	56	780	970	-24

III. Distribution of AOX and TOC in total and fractionated samples before and after biological treatment

	AOX, mg/L									TOC, mg/L								
	In			Out			% Removal			In			Out			% Removal		
Source	Total	<1kD	>1kD	Total	<1kD	>1kD	Total	<1kD	>1kD	Total	<1kD	>1kD	Total	<1kD	>1kD	Total	<1kD	>1kD
C(EO)	157	98	59	111	66	45	29	33	24	626	286	340	526	138	388	16	52	-14
(D50+C50)EO	92	45	47	67	15	52	27	67	-11	527	232	295	474	108	366	10	53	-24
D(EO)	34	25	9	23	11	12	32	56	-33	407	176	231	351	133	218	14	24	6
OC(EO)	83	35	48	61	18	43	27	49	10	395	159	236	266	74	192	33	53	19
O(D50+C50)+Eo	65	39	26	39	26	12	42	33	54	397	154	243	285	76	209	28	51	14
OD(EO)	16	8	8	11	4	7	31	50	13	325	131	194	201	66	135	38	50	30

(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 min or 15 min. A high EC_{50} indicates low toxicity. The Microtox test has been correlated with fish toxicity (*22, 23*).

Ultrafiltration

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

Results and discussion

The pollution load from the combined C- and EO-stage effluents, before and after treatment, is reported in **Table II**. The percent removal of a particular pollutant by aerobic treatment is the difference in the quantity before and after treatment in relation to the initial quantity. The percent removal due to increasing substitution is the difference between pollutant quantity from the substituted and unsubstituted effluents, relative to the unsubstituted effluent. The percent removal resulting from oxygen delignification is the difference in pollutant level from sequences with and without oxygen delignification at the same ClO_2 substitution level in relation to the oxygen-free sequence.

COD, BOD, and degree of toxicity decreased as ClO_2 substitution increased; they also decreased with addition of biological treatment or oxygen delignification.

COD

Biological treatment, oxygen delignification, and ClO_2 substitution decreased the COD in the bleach-plant effluent (Table II). Biological treatment of the effluents reduced COD by an average of 35%. Oxygen delignification decreased COD by an average of 41%, and substitution with 100% ClO_2 caused an average reduction of 24%. The reduction due to inclusion of oxygen delignification can be attributed to a removal of 45% of the lignin entering the chlorination stage. All data were subjected to a standard ANOVA test with a 95% confidence level to determine if these decreases in COD were statistically significant. The results showed that biological treatment, oxygen delignification, and increasing ClO_2 substitution significantly reduced COD.

BOD

Biological treatment removed an average of 82% of the initial BOD. Oxygen delignification reduced BOD by an average of 41%, and 100% ClO_2 substitution in the chlorination stage decreased BOD by an average of 42%. The decrease in BOD as substitution increased is probably due to the protective nature of ClO_2 toward cellu-

lose. The decrease from oxygen delignification is due to the removal of additional organics. ANOVA analysis indicated that BOD reduction associated with aerobic treatment was significant, and the decreases associated with oxygen delignification and ClO_2 substitution were statistically significant if only the pretreatment BOD was analyzed.

TOC

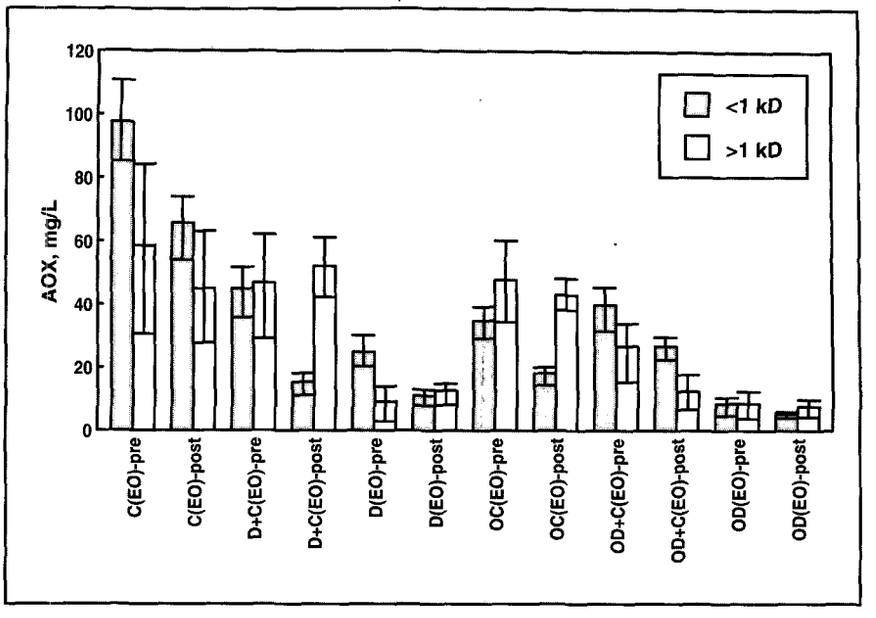
The TOC (total organic carbon) includes all organic carbon compounds in the effluent regardless of their chemical structure. For the total effluent, TOC was reduced an average of 23% by aerobic treatment, as seen in **Table III**. However, this reduction was 20% higher in sequences containing oxygen delignification. For all effluents, aerobic treatment reduced the low-molecular-weight components by an average of 47%, while the high-molecular weight components showed no significant reduction in TOC (15%). This result was expected because of the resistance to treatment of high-molecular-weight compounds.

In oxygen-containing sequences, the total TOC reduction with 100% ClO_2 in the chlorination stage was only 18%. However, TOC was reduced an average of 35% in the non-oxygen sequences. The large difference in the reduction between the oxygen and non-oxygen-containing sequences was due to the removal of organic material by the oxygen-delignification process. For all effluents, 100% ClO_2 substitution reduced total TOC by 26%, and oxygen delignification reduced total TOC by 27%. Reductions in TOC from oxygen delignification, ClO_2 substitution, and biological treatment caused significant reductions in TOC at the 95% confidence level.

AOX

AOX decreased as a result of oxygen delignification, ClO_2 substitution, and biological treatment, as seen in Table III and as illustrated in **Fig. 1**. ClO_2 substitution reduced total AOX by an average of 80%. Biological treatment reduced total AOX by an average of 32%, and the inclusion of oxygen delignification reduced total AOX an average of 41%.

1. Distribution of AOX in simulated bleach-plant effluent



Reduction in AOX by ClO_2 substitution was caused by an increase in oxidation reactions and a decrease in elemental chlorine. Oxygen delignification reduced total AOX by removing organics that would otherwise be available for substitution reactions (*24*). ANOVA showed that reductions by oxygen delignification, ClO_2 substitution, and biological treatment were significant at the 95% confidence level.

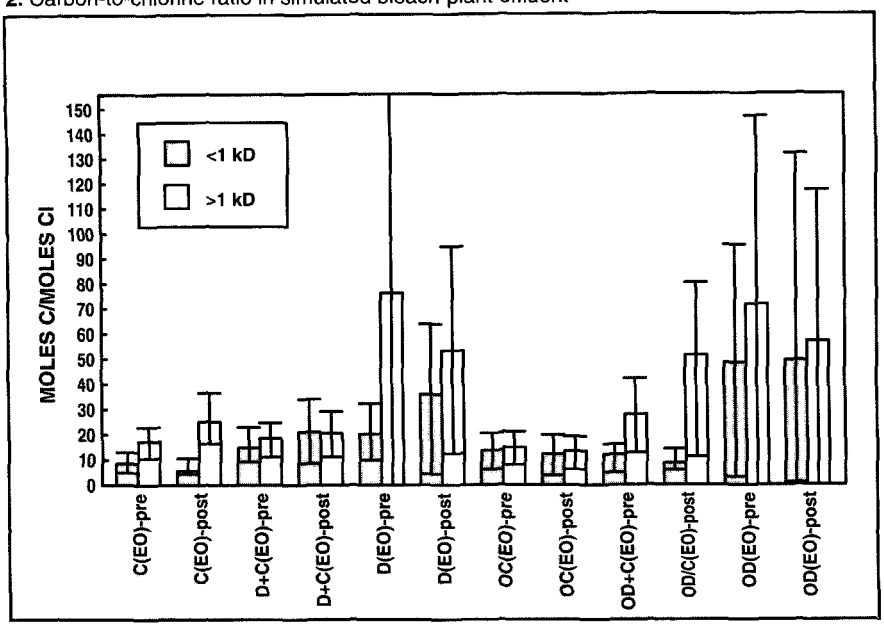
The impact of AOX compounds on the environment is unclear in many respects, but it depends in part on the molecular weight of the specific compound. Low-molecular-weight compounds have the potential to enter the cell, cause toxicity, and bioaccumulate in the fatty tissue of aquatic species (*11*). A correlation between low-molecular-weight AOX and toxicity to trout and daphnia (r^2 = 0.68 and 0.82, respectively) was found by Bryant and Amy (*25*).

In order to examine these effects, the total AOX was partitioned into a low (<1 kD) and a high (>1 kD) fraction. The high-molecular-weight AOX is calculated as the difference between the total and the low-molecular-weight AOX. Upon partitioning, an average of 56% of the AOX was contained in the low-molecular-weight fraction (Table III). Of these low-molecular-weight compounds, 48% were removed by aerobic treatment.

For two of the samples tested, the high-molecular-weight AOX apparently increased after biological treatment. Upon statistical evaluation, however, the apparent increase is not significant. The error bars depicted in Fig. 1 estimate the 95% confidence interval for each AOX fraction based on analytical variances. The intervals for the points in question overlap, indicating that there is no statistical evidence that the two samples are different from each other. Further inspection shows that the confidence intervals for all high-molecular-weight fractions overlap. Thus, there is no statistical difference between the inlet and outlet samples, and no conclusion can be drawn about the removal efficiency in the high-molecular-weight fraction. Inlet and outlet low-molecular-weight AOX are statistically different by the same inspection method.

The degree of chlorine substitution, as represented by the C/Cl ratio, is calculated as the ratio of TOC to AOX of each sample (*19*). **Figure 2** shows

2. Carbon-to-chlorine ratio in simulated bleach-plant effluent



that, with a few exceptions, the C/Cl ratio increased following biological treatment, indicating that there is less AOX relative to TOC. At the points where the C/Cl ratio decreased after treatment, a larger reduction is seen in the TOC relative to the AOX. Thus, the decrease is attributable to the larger decrease in effluent TOC. Since this result was contrary to the expected increase in the C/Cl ratio after biological treatment, a statistical analysis was performed.

The error bars shown in Fig. 2 indicate the 95% confidence interval based on analytical variance. The extremely large intervals seen on some points are due to the assumption that the samples are statistically independent. If the covariance between the TOC and AOX could be estimated, the confidence intervals would become smaller. At the present time, these intervals indicate that the decreases in the C/Cl ratio between the pre-and post-biological treatment conditions in some samples are not statistically significant. In all but one case, there is no statistical difference between the pre- and post-treatment samples in the high-molecular-weight range.

Biological treatment did not always increase the C/Cl ratio because TOC includes all organic carbon, whether or not it is aromatic in nature. Oxygen delignification and aerobic treatment lead to a general decrease of chlorinated and nonchlorinated organics. Therefore, the changes in C/Cl ratio resulting from biological treatment and oxygen delignification were not significant at the 95% confidence level. The C/Cl ratio is, therefore, considered constant within the effluents. ClO_2 substitution, however, increased the C/Cl ratio by a selective decrease in AOX. Changes in the C/Cl ratio by ClO_2 substitution were significant at the 95% confidence level.

Color

Color was not removed by biological treatment methods, as seen in Table II. Thus, reductions in color must depend on bleach-process modifications. The inclusion of oxygen delignification reduced color by an average of 67%, while increasing ClO_2 substitution to 100% decreased color by an average of 61%. Reductions by both oxygen delignification and ClO_2 substitution were significant when subjected to ANOVA analysis, whereas biological treatment was not.

Toxicity

ClO_2 substitution (100%), oxygen delignification, and biological treatment caused an average toxicity reduction of 60%, 39%, and 43%, respectively. The addition of oxygen delignification to the conventional bleaching sequence resulted in a much lower level of toxicity, as seen in Table II. In fact, the toxicity of effluents from oxygen-containing sequences before biological treatment was similar to or below that of the treated effluent for the conventional sequence. This same trend is observed for COD, TOC, and AOX. Thus, inclusion of an oxygen stage before a conventional bleach sequence can reduce the environmental impact of discharged effluents. The results showed that the main effects of biological treatment, oxygen delignification, and increasing ClO_2 substitution were all significant.

Treatment effectiveness

As seen in Tables II and III, biological treatment efficiency can be affected by the inclusion of oxygen delignification and ClO_2 substitution. The quantity of organics that are easily removed by biological oxidation, as measured by the ratio of BOD to COD, indicates the ease of effluent treatment. A high ratio indicates that the effluent is more susceptible to aerobic treatment. If the ratio of BOD to COD is examined for the inlet effluent of each sequence, the oxygen-delignified pulps have a higher ratio than the conventional effluents. However, this ratio is still well under 25%, indicating that aerobic treatment may not be the most effective treatment method (*26*).

In most cases, the percent reduction in pollutant load after biological treatment was higher for effluents from oxygen-containing sequences at the same ClO_2 substitution level. BOD was an exception, since the experimental method terminated all biological treatments at a constant BOD. The reductions noted are due to a significant decrease in initial pollutant concentration for effluents from oxygen-containing sequences. The oxygen stage

lowered initial pollutant load by an average of 45% compared with a similar sequence without oxygen. However, the absolute amount actually removed by biological treatment, at a given percent ClO_2, remains comparable between the oxygen-bleached and conventionally bleached effluents.

The percent reduction in pollutant load before biological treatment, as a function of ClO_2 substitution, showed a similar decrease for both oxygen-containing and conventional sequences. However, the percent reduction attributable to biological treatment as ClO_2 substitution increased yielded no consistent pattern. Therefore, ClO_2 substitution does not affect the treatability of bleach-plant effluents. The environmental benefit is realized in the reduction of initial amount of pollutants, especially toxicity.

Conclusions

The results support the following conclusions.

1. The addition of oxygen delignification before (D+C)(EO)D bleaching can reduce the quantity of BOD, COD, AOX, color, TOC, and toxicity of bleach-plant effluents.
2. Increasing levels of ClO_2 substitution in the chlorination stage can reduce BOD, COD, AOX, color, TOC, and toxicity.
3. Biological treatment is effective in reducing BOD (70–90%), COD (27–45%), AOX (27–45%), toxicity (16–56%), and TOC (16–38%), but it has no effect on color.
4. ClO_2 substitution does not affect the efficiency of effluent treatment.
5. The percentage of COD removed from effluents during biological treatment is higher for bleach sequences with oxygen delignification than for conventional bleach sequences. However, the absolute amount of COD removed is lower.
6. The absolute and relative amounts of BOD removed from effluents during biological treatment are lower for bleach sequences with oxygen delignification than for conventional bleach sequences.
7. Biological treatment removes a much higher percentage of the toxicity for bleach sequences preceded by oxygen delignification than for conventional sequences. The absolute removal of toxicity is very similar for the oxygen-delignified and conventional sequences.
8. The percent removal and the absolute removal of total AOX is the same for both the conventional and the oxygen-delignified sequences. TJ

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