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TRANSFORMATIONS OF WASTEWATER DURING BIOLOGICAL TREATMENT

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ABSTRACT

The efficiency of wastewater treatment plants needs to be optimized as mills are directed to discharge cleaner effluents. In order to achieve this objective, a clear understanding about the processes that produce clean effluents is needed. The purpose of these studies was to examine the transformations of wastewater during biological treatment. A bench scale laboratory reactor was designed and constructed so that sequential transformations of wastewater constituents could be monitored as they underwent biotic and abiotic processes similar to those occurring in facultative lagoons. The levels of AOX, TOC, COD, solids, and molecular weight distributions were monitored for two different whole mill wastewaters.

Primary removal mechanisms for most constituents of whole mill wastewaters appear to be rapid and operate under aerobic conditions. Prolonged exposure to anaerobic conditions can effect further dehalogenation with little organic carbon mineralization. In some cases, although concentrations of AOX were low, the organic carbon remaining in treated effluents was more highly chlorinated than the influents. Changes in oxidation levels of the organic carbon in wastewaters were not detected, suggesting concurrent oxidative and reductive mechanisms of carbon mineralization. Lower molecular weight organic carbon is preferentially removed. While compounds with an apparent MW \leq 960 are removed, the apparent molecular weight limit for the most effective biodegradation is close to 300 daltons.

INTRODUCTION

As mills are pressured to discharge cleaner effluents, it is important to extract as much efficiency as possible from wastewater treatment plants. In order to optimize conventional wastewater treatment plant operations, it is necessary to understand the transformations organic waste undergoes during treatment. Characterization of the recalcitrant constituents of pulp and paper mill wastewater could provide clues to ways of improving efficiency. Furthermore, information about the composition of discharged effluents facilitates the evaluation of potential environmental impacts.

Several parameters are commonly measured in wastewaters as a means to characterize them and to estimate their environmental effects. Oxygen demand parameters, of course, are critically important in determining whether effluents can cause oxygen depletion in a receiving water body. A basic measure of the strength of an effluent is provided by total organic carbon (TOC) concentrations. Removal of TOC by treatment will result in a reduction in the absolute amount of organic waste that is discharged, which will lower the probability of significant environmental effects. However, TOC levels do not necessarily correlate with environmental impact. For example, selective removal of innocuous TOC could leave harmful constituents in wastewater with no real change in potential impacts.

The level of chlorination of the organic substances in wastewaters is an issue of great importance to the pulp and paper industry. A high degree of chlorination in organic compounds has been correlated with toxicity (1,2) and the propensity for bioaccumulation (3). Proposed regulations for AOX (adsorbably organic halogen) in effluents will drastically limit the production and discharge of chlorinated organic material (4). Thus, extensive dehalogenation is a highly desirable function of wastewater treatment.

The molecular size of wastewater constituents may affect their ability to be removed by physical, chemical, and biological methods. To a large extent, the biodegradability of a compound is dependent on its bioavailability. To be bioavailable, a compound must be able to enter a bacterial cell. Transport across cell membranes is limited by physical characteristics of the compounds, one of which is molecular weight. Passive hydrophobic transport across cell membranes is limited by solubility in lipids, which in turn is limited by molecular weight. Passive hydrophilic transport across cell membranes is limited by molecular size, and in general is restricted to compounds less than 500 daltons (5). The presence of extracellular enzymes may contribute to degradation of compounds that are unable to penetrate a cell wall.

The purpose of these studies was to obtain information about the transformations of wastewater during biological treatment. The sequential changes in the concentrations of AOX, TOC, COD, solids and the changes in molecular weight distributions were monitored during laboratory treatment of two different whole mill wastewaters.

EXPERIMENTAL

Laboratory Reactor

A bench scale laboratory reactor was designed and constructed so that sequential transformations of wastewater constituents could be monitored as they underwent biotic and abiotic processes similar to those occurring in a facultative lagoon. The dimensions of the cylindrical, acrylic reactor are given in Figure 1. A baffle directed the flow through the full volume of the reactor. Six equidistant ports provided sites for sequential sampling. The reactor volume was 22 L, and there was a continuous, arbitrary flow (6) of whole mill effluents, varying between 1.1 and 1.4 mL/min, which resulted in a mean hydraulic retention time of 11 to 14 days. A diffuser placed 25 cm below the water surface provided aeration and mixing. Air was supplied at an approximate rate of 1 L/min. Initially, the reactor was supplied with sludge solids obtained from a facultative lagoon that treated wastewater from an integrated mill utilizing hardwood and a C/D(EO)HDED bleaching sequence. The sludge was allowed to settle in the bottom 8 cm of the reactor. After more than one year of operation, there was no obvious increase in sludge levels, suggesting endogenous respiration of bacterial biomass and digestion or compression of nonbiological solids.

The reactor had been in operation for 6 months prior to the first sampling reported in this paper and for 10 months when the second set of samples was obtained. Measurements of COD and pH were used to monitor the reactor's health and its approach to acclimation and steady state. The constancy of the values were evaluated and compared to values obtained by the mills from which the wastewaters were obtained.

Wastewaters

During the first several months of operation, the reactor was fed wastewaters obtained bimonthly from the same mill that provided the sludge. The wastewaters were sampled (24 hour composites) from the mill at the inflow to the secondary lagoon after clarification and nutrient addition; these wastewaters were quite variable with respect to AOX, TOC, and COD levels over 6 months. These variable influent values were reflected in variable reactor effluent values, as is typical with mill lagoons (7). However, prior to collecting the samples reported here, a single source of influent was fed to the reactor for at least two weeks. Thus, the observed changes reflect true transformations in wastewater constituents and not simply changing influent characteristics. The samples were shipped overnight on ice and stored at 4° C until they were used. Four liter aliquots were allowed to come to room temperature over several hours and then fed to the reactor while being stirred.

The second wastewater that was treated in the laboratory was obtained as a single grab sample from the inflow of a secondary lagoon from a primarily softwood (90%) pulp mill utilizing a D(EOP)DED bleach sequence. The samples were refrigerated with a maximum storage time of 4 weeks before use.

Sampling and Analyses

The wastewater obtained from the hardwood mill with a C/D(EO)HED sequence is designated C-HW. The reactor was sampled two times, 1 day apart, after the reactor had been fed with this influent for 2 weeks. The wastewater obtained from the softwood mill with a D(EOP)DED sequence is designated D-SW. The reactor was sampled two times, 8 days apart, after the reactor had been fed with this influent for 3 weeks.

A sample set included the influent (sampled before introduction to the reactor), approximately 100 mL aliquots taken from each of the six sampling ports, and a composited effluent (usually 1 day). Typical estimated mean hydraulic retention times (based on plug flow), at each of the ports are as follows: Port 1 - 2 days, Port 2 - 4 days, Port 3 - 6 days, Port 4 - 8.25 days, Port 5 - 9.75 days. Port 6 - 11.25 days, and at the outflow - 12.75 days. Just before sampling, the dissolved oxygen was measured at the ports and at other locations by submerging a sealed YSI Model 5750 BOD probe (YSI Model 54 ARC D.O. meter) at appropriate levels in the reactor. The pH was measured of the whole effluents immediately after sampling. To measure solids and soluble constituents, selected samples were filtered through 934-AH glass microfiber filters (1.5 μ m).

The AOX was measured in triplicate by a batch method based on SCAN-W 9:89, using a Dohrman Model DX-20 TOX Analyzer. The TOC was measured by acidifying diluted samples to pH < 2 with sulfuric acid, purging with nitrogen, and analyzing in triplicate with a Shimadzu Model 5050 TOC Analyzer. For the C-HW samples, chemical oxygen demand was measured in duplicate by adding aliquots of a diluted sample to prepared dichromate solutions (Bioscience), digesting, and measuring the absorbance at 600 nm. Potassium hydrogen phthalate was used to construct a standard curve. Duplicate or triplicate COD measurements were made of the undiluted D-SW samples using a similar method, but with different prepared solutions of dichromate (Hach). Total suspended solids and volatile suspended solids were analyzed by standard methods (8). Due to practical limits of the volumes that could be sampled, single replicates were analyzed.

The molecular weight distributions were determined by a recently developed method using medium pressure gel permeation chromatography coupled with detection by total organic carbon analyses (9,10). A series of two Sephadex columns (G-50 and G-15 gels) was eluted with 0.1 N LiCl directly into a TOC analyzer placed in a continuous sampling

mode which resulted in a TOC measurement every 3-4 minutes. Polyethylene glycol standards were used to relate retention time to weight-averaged molecular weights.

RESULTS AND DISCUSSION

pH and Dissolved Oxygen

The pH and the DO levels throughout the reactor are given for the two different wastewaters in Figure 2. There was an immediate increase of approximately one pH unit for both wastewaters, which has been observed in mill lagoons (11). The DO profile was different during the samplings for the two wastewaters despite the fact that aeration levels were similar and COD loadings were comparable. The first wastewater examined, the C-HW wastewater, reduced the oxygen level in the reactor to anaerobic levels by Port 3; the water column remained anoxic (≤ 1 ppm) until discharge from the reactor. By contrast, the D-SW wastewater more gradually reduced the oxygen level. However, there was a very steep DO gradient just below Ports 3 and 4 (at the bottom of the reactor); at approximately 2 cm below Ports 3 and 4, the DO levels were \leq 0.2 ppm. It is likely that the C-HW wastewater was exposed to anaerobic conditions for longer times than the D-SW wastewater. It is possible that more algal growth in the more mature reactor promoted oxygenation by photosynthesis during the day (when these samples were taken) when the D-SW wastewater was being treated. Another possibility is that the BOD/COD ratio for D-SW was significantly lower than for the C-HW wastewater; i.e., less of the organic material was biodegradable in the former, and therefore, less oxygen was consumed. Although measurements of BOD were not conducted to verify this possibility, a lower TOC reduction for the D-SW wastewater is consistent.

Reduction in AOX, TOC, COD, Solids

The values for soluble and whole AOX, TOC, and COD and for solids at the different sampling sites are given in Tables 1 and 2 for the two wastewaters; the same data are given in terms of percent reductions in Figures 3-5. Removal efficiencies were typical of those reported in aerated stabilization basins in mills (11-14).

A significant feature of these reduction curves is that in most cases, the majority of the removal occurs by the first or second sampling port. Thus, primary removal mechanisms appear to be rapid and operate under aerobic conditions for all of the parameters. Under these conditions, only small increases in efficiency appear to be possible with extended hydraulic retention times. The reasonably rapid removal is supported by other laboratory investigations into aerobic biological removal of AOX (15) and COD (16), where substantial amounts of removal occurred within a matter of hours. However, there is some discrepancy in these findings with other work in which correlations have been found between hydraulic retention time in a lagoon and removal efficiencies. It is possible that longer retention times cause incremental increases in efficiency that are highly dependent on whether anaerobic or aerobic conditions predominate. Whereas aerobic processes occur quickly, prolonged exposure may be required for anaerobic processes. During the treatment of the C-HW wastewater, most of the AOX was removed, and all of the TOC was removed in the aerobic conditions at Ports 1 and 2. However, there was still a significant decrease in AOX as the wastewater traveled to the anaerobic conditions at Ports 3 and 4. There was no accompanying decrease in TOC. These results are consistent with the occurrence of anaerobic dehalogenation in which chlorine is removed as chloride and replaced by hydrogen, and there is no mineralization of the carbon. The more anoxic conditions in the reactor during treatment of the C-HW wastewater compared to the conditions during the treatment of the D-SW wastewater may have contributed to better AOX reduction by allowing more extensive anaerobic dehalogenation to take place.

Settling of influent solids was a possible removal mechanism for whole wastewater constituents. This mechanism should be differentiated from biosorption of wastewater constituents onto virgin biomass followed by settling of biological solids (17). For the D-SW influent, 20% of the TOC in the whole samples was in the form of particulate TOC, as calculated by the difference between whole and filtered samples. By Port 1, both TOC and TSS were substantially reduced. Out of the 51% removal of whole TOC, 16% was due to settling of solids and 35% could be ascribed to other mechanisms (corresponding to a 44% reduction in soluble TOC). At the outflow, there was no detectable difference in TOC concentrations between the filtered and whole samples; therefore, the 20% particulate TOC that was initially present was completely removed. Although the overall TSS concentrations and reductions of the C-HW wastewater were similar to the D-SW wastewater, the solids composition was clearly different. A much lower %VSS indicated a higher inorganic content, and therefore, only about 4% of the total whole TOC removal at the outflow could be attributed to settling; 75% of the reduction was due to other mechanisms (corresponding to a 79% reduction in soluble TOC).

Settling of solids accounted for 13% of the 42% whole AOX removal in the D-SW wastewater; 29% of the removal was due to other mechanisms (corresponding to 35% removal of soluble AOX). In the C-HW wastewater treatment, 7% of the whole AOX removal was due to solids removal, leaving 54% due to other mechanisms (corresponding to 58% removal of soluble AOX). Using VSS concentrations as a measure of particulate organic carbon, it is interesting to note that the concentration of organic chlorine in the organic fraction of the C-HW particulates (3.7 mg Cl/g VSS) was lower than for the D-SW particulates (5.2 mg Cl/g VSS).

It should be recognized that solids concentration in wastewaters is highly variable and no special care was taken during mill sampling of these wastewaters to get representative solids samples. This information is provided in order to illustrate that the settling of solids may have variable effects on removal of whole wastewater constituents.

Chlorine to Carbon Molar Ratio

The ratio of chlorine to carbon in wastewater is a crude estimation of potential environmental impact. For all of the whole wastewaters and three fourths of filtered wastewaters, treatment caused a significant increase in chlorine to carbon ratios (Figures 6 and 7). An overall preferential removal of nonchlorinated organic compounds is suggested. The effect was most pronounced for whole C-HW wastewaters. In other studies, constant or reduced Cl/C ratios have been reported (11,18). However, close examination of the data of Bryant et al. (7) shows that there is an increase in the Cl/C for constituents with a MW \leq 500. Furthermore, initial AOX levels in whole effluents in the other investigations were 3-30 times higher than for the wastewaters in this study, suggesting different compositions.

The pattern of changes in Cl/C for the C-HW wastewater is shown in Figure 6. There is an immediate substantial increase as organic carbon is rapidly removed; chlorine is also removed, but not to the same extent. When the wastewater travels to the portion of the reactor where anaerobic dehalogenation is expected to take place, the Cl/C ratio decreases corresponding to AOX reduction with constant TOC levels. However, the Cl/C ratio of the wastewater effluents does not ever reduce to the level of the influent. It appears that aerobic treatment removes organic carbon more effectively than organic chlorine, and that subsequent anaerobic mechanisms counteract this preference.

For the D-SW wastewater, there is a significant increase in the Cl/C of the effluents compared to the influent, but the effect is not nearly as large as for the other wastewater. These results suggest that the chemical characteristics of the organic chlorine in wastewaters will dictate which mechanisms will predominate in its destruction.

COD to TOC Ratio

The molar ratio of COD to TOC (O₂ to C) is an indication of the average oxidation level of the organic carbon in a complex mixture. For example, one mole of oxygen would be required to oxidize each of the six carbons in glucose (assuming COD equals the theoretical oxygen demand) giving a COD/TOC of 1.0; the theoretical COD/TOC for vanillin is 1.1 and for chloromuconic acid (an expected aerobic biodegradation product of chlorobenzoic acid and similar to products from lignin bleaching) is 0.9. For the wastewaters examined in this work, the means ranged from 0.9 to 1.4 (Figure 8). There were generally no significant differences as determined by comparison of 95% confidence intervals. It is interesting that there were no substantial changes in the oxidation state of the remaining organic carbon throughout treatment. This implies that mineralization of carbon must occur by a variety of mechanisms that do not result in a substantial change in overall chemical structure. For example, TOC loss primarily by way of decarboxylation would result in a decrease in oxidation level (or increase in COD/TOC); therefore, if this mechanism occurs, it must occur concurrently with mechanisms that increase the oxidation level, such as ring cleavage or hydroxyl substitution (19-21).

Molecular Weight Distributions

The filtered D-SW wastewater was fractionated by molecular The chromatogram of the influent, effluent, and size. intermediately treated wastewaters is given in Figure 9. The majority of the organic carbon that was removed had a molecular weight below 1000 daltons. The areas of the curve that fell between the peaks of the standards were integrated to provide discrete ranges of MW. The reductions of TOC within each molecular weight division are given in Figure 10. It should be noted that polyethylene glycol standards are likely to be chemically dissimilar to wastewater constituents so absolute molecular weights may not be accurate. However, it is clear that the smallest compounds were the most readily removed. A small quantity of the very largest constituents $(MW \ge 10,900)$ in the influent was also removed. There was a small increase in TOC between molecular weights 331 and 960 when the wastewater traveled from Port 2 to the outflow. The increase could result from cellular exudates or from a small amount of polymerization of the lower weight material. The latter phenomenon has been observed elsewhere in pulp mill wastewaters (11).

Despite the large reduction in low molecular weight compounds by biological treatment, the effluent still comprises mostly compounds with a molecular weight \leq 960, which is consistent with the finding of Jokela et al. (11). The proportion of TOC with MW \leq 960 before treatment is 78% and after treatment it is 67%. The fraction which exhibits the most depletion is the very lowest molecular weight material, which is readily seen by the substantial reduction in the size of the peak eluting at 240 minutes in Figure 8. Before treatment, 27% of the influent TOC is composed of compounds with an apparent MW \leq 106; after treatment that fraction is 9%.

The biological removal of the low molecular weight organic carbon is consistent with other researchers who have found preferential removal of low molecular weight AOX as well as TOC (11,12,18). The parallel reductions of TOC and AOX in different molecular weight fractions suggest that chlorine and carbon are degraded together primarily by biodegradation; restrictions of molecular size are likely to be an important limiting factor in biological removal of organic halide and carbon. The molecular weight limit for effective biodegradation appears to be close to 300 daltons.

CONCLUSIONS

Primary removal mechanisms for most constituents of whole mill wastewaters appear to be rapid and operate under aerobic conditions. Maximum removal of organic carbon is reached by 2-4 days in aerobic conditions. Organic halide is substantially removed under the same conditions, but subsequent prolonged exposure in anaerobic conditions can effect further dehalogenation without organic carbon mineralization. The result is a corresponding fluctuating chlorine to carbon ratio. For these wastewaters, the chlorine to carbon ratios of the final, fully treated wastewaters are higher than the influents, which indicates an ultimate preferential removal of nonchlorinated organic carbon. Although substantial quantities of both organic carbon and organic halide are removed during treatment, in some cases, the organic carbon remaining after treatment is more highly chlorinated than in the influent.

There were no significant changes in the average oxidation level of the organic carbon in the wastewaters, even when traveling between aerobic and anaerobic zones. These results suggest that mineralization reactions that reduce the oxidation level, such as decarboxylation, must occur concurrently with reactions that oxidize the organic carbon.

Settling of solids may be a significant removal mechanism of whole wastewater AOX, TOC, and COD for some types of wastewaters. However, solids composition and levels are variable depending on the wastewater sources, and therefore, the potential for removal is expected to be quite variable.

The majority of the organic carbon that is removed has an apparent molecular weight less than 960. Furthermore, within this weight fraction of organic carbon (MW \leq 960) it appears that the lower the molecular weight, the more readily carbon mineralization occurs. The limit for the most effective biodegradation appears to be close to 300 daltons.

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		Influent	Port 1	Port 2	Port 3	Port 4	Port.5	Port 6	Effluent
Whole	(1) ^b (2)	231±4 -	112 ± 4 -	119±5 -	115 ± 7 -	110 ±8 -	105 ± 4	104 ± 7	95 ± 2
Filtered	(1)	185 ± 12 185 ± 12	103 ± 6 132 ± 6	99 ± 4 93 ± 11	106 ± 5 94 ± 9	98 ± 4 109 ± 10	95 ± 15 110 ± 6	102 ± 3 96 ± 4	100 ± 7 89 ± 9
Whole	(1) (2)	5.2 ± 0.3 -	3.8 ± 0.3 -	3.1±0.2 -	3.0 ± 0.2 -	2.9 ± 0.2 -	2.9 ± 0.2 -	3.1 ± 0.3 -	3.0 ± 0.3
Filtered	(2)	4.3 ± 0.2 4.3 ± 0.2	3.1 ± 0.3 3.0 ± 0.3	2.9 ± 0.2 3.1 ± 0.2	3.2 ± 0.3 3.0 ± 0.3	2.6±0.3 3.1±0.3	2.8 ± 0.2 3.1 ± 0.3	2.8 ± 0.2 3.2 ± 0.2	2.8 ± 0.3 4.1 ± 0.3
Whole	c	1097 ± 140	374 ± 45	365 ± 70	360 ± 45	361 ± 0	354 ± 63	354 ± 25	326 ± 76
Filtered	(1) ^c (2)	710±13 710±13	335 ± 89 328 ± 12	338 ± 70 335 ± 29	338 ± 13 332 ± 12	335±0 331±12	325 ± 51 328 ± 13	324 ± 6 328 ± 6	306 ± 114 330 ± 26
	(2)	217 -	42	37	33	35	26 -	27	17
	(2) (2)	175	29	25	24	23	- 16	- 16	· 0
InfluentPort IPort 2Whole $(1)^b$ 231 ± 4 112 ± 4 119 ± 5 Filtered (1) 185 ± 12 103 ± 6 99 ± 4 (2) 185 ± 12 103 ± 6 99 ± 4 Whole (1) 5.2 ± 0.3 3.8 ± 0.3 3.1 ± 0.2 (1) 5.2 ± 0.3 3.8 ± 0.3 3.1 ± 0.2 Filtered (1) 4.3 ± 0.2 3.1 ± 0.3 2.9 ± 0.2 Whole c 1097 ± 140 374 ± 45 365 ± 70 Filtered $(1)^c$ 710 ± 13 328 ± 12 335 ± 29 (1) 217 42 37 (2) 217 42 37 (2) 175 29 25 (1) 175 29 25 (1) 175 29 25	Whole Filtered Whole Filtered		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Influent (1) ^b 231 ± 4 (2) - (1) 185 ± 12 (2) 185 ± 12 (1) 5.2 ± 0.3 (2) - (1) 5.2 ± 0.3 (2) - (1) 5.2 ± 0.3 (2) - (1) 4.3 ± 0.2 (2) 710 \pm 13 (2) 710 \pm 13 (1) 217 (1) 217 (1) 217 (2) - (1) 217 (2) - (1) 217 (2) - (1) 217 (2) - - - (1) 217 - - (1) 217 - - (2) - - - - - - - - - - - -	Influent Port1 (1) ^b 231 ± 4 112 ± 4 (2) - - (1) 185 ± 12 103 ± 6 (2) 185 ± 12 103 ± 6 (2) 185 ± 12 132 ± 6 (2) 5.2 ± 0.3 3.8 ± 0.3 (2) 4.3 ± 0.2 3.1 ± 0.3 (2) 4.3 ± 0.2 3.1 ± 0.3 (2) 4.3 ± 0.2 3.0 ± 0.3 (1) 4.3 ± 0.2 3.0 ± 0.3 (2) 710 ± 13 325 ± 89 (2) 710 ± 13 328 ± 12 (1) 217 42 (2) 710 ± 13 328 ± 12 (2) 217 42 (2) -175 29 (1) 175 29	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	InfluentPort.lPort.2Port.3(1)b 231 ± 4 112 ± 4 119 ± 5 115 ± 7 (2) 231 ± 4 112 ± 4 119 ± 5 115 ± 7 (2) 185 ± 12 103 ± 6 99 ± 4 106 ± 5 (1) 5.2 ± 0.3 3.8 ± 0.3 3.1 ± 0.2 3.0 ± 0.2 (1) 5.2 ± 0.3 3.8 ± 0.3 3.1 ± 0.2 3.0 ± 0.2 (2) 4.3 ± 0.2 3.1 ± 0.3 2.9 ± 0.2 3.2 ± 0.3 (2) 4.3 ± 0.2 3.1 ± 0.3 2.9 ± 0.2 3.2 ± 0.3 (2) 4.3 ± 0.2 3.1 ± 0.3 2.9 ± 0.2 3.2 ± 0.3 (2) 4.3 ± 0.2 3.1 ± 0.3 3.1 ± 0.2 3.0 ± 0.2 (2) 710 ± 13 335 ± 89 3.8 ± 70 360 ± 45 (1) 217 42 37 33 (1) 217 42 37 33 (1) 175 29 25 24	InfluentPort.1Port.2Port.3Port.4(1)b 231 ± 4 112 ± 4 119 ± 5 115 ± 7 110 ± 8 (2) 185 ± 12 103 ± 6 99 ± 4 106 ± 5 98 ± 4 (2) 185 ± 12 132 ± 6 93 ± 11 94 ± 9 109 ± 10 (1) 52 ± 0.3 3.8 ± 0.3 3.1 ± 0.2 3.0 ± 0.2 2.9 ± 0.2 (2) 4.3 ± 0.2 3.1 ± 0.3 2.9 ± 0.2 3.2 ± 0.3 2.6 ± 0.3 (1) 4.3 ± 0.2 3.1 ± 0.3 3.1 ± 0.2 3.0 ± 0.3 3.1 ± 0.3 (2) 710 ± 13 335 ± 89 338 ± 70 360 ± 45 361 ± 0 (1) 217 42 37 33 35 35 (1) 217 42 37 33 35 (1) 175 29 25 24 23	InfluentPort 1Port 2Port 3Port 4Port 4(1)231 ± 4 112 ± 4 119 ± 5 115 ± 7 110 ± 8 105 ± 4 (2)185 ± 12 103 ± 6 99 ± 4 106 ± 5 98 ± 4 95 ± 15 (1)5.2 \pm 0.3 3.8 ± 0.3 3.1 ± 0.2 3.0 ± 0.2 2.9 ± 0.2 2.9 ± 0.2 2.9 ± 0.2 (1)5.2 \pm 0.3 3.1 ± 0.3 3.1 ± 0.2 3.0 ± 0.3 3.1 ± 0.2 3.0 ± 0.3 2.6 ± 0.3 2.8 ± 0.2 2.9 ± 0.2 (1) 4.3 ± 0.2 3.1 ± 0.3 3.1 ± 0.2 3.0 ± 0.3 3.1 ± 0.3 (1) 4.3 ± 0.2 3.1 ± 0.3 3.1 ± 0.2 3.0 ± 0.3 3.1 ± 0.3 3.2 ± 1.3 3.2

TOC ^a (mg/L)	Whole	(1) ^b	226 ± 6 264 ± 5	60 ± 3 78 ± 4		60 ± 4 63 ± 3	FUEL2 FOEL3 60±4 64±3 63±3 59±4		Furt.3 64 ± 3 59 ± 4
	Filtered	(1) (2)	213 ± 6 254 ± 5						
AOX ^a (mg/L)	Whole	(1)	10.4 ± 0.9 10.6 ± 0.7	6.5 ± 0.2 6.5 ± 0.3	6.1 ± 0.2 6.2 ± 0.3).2).3).2 4.7±0.7).3 4.3±0.4		4.7 ± 0.7 4.3 ± 0.4
	Filtered	(1) (2)	9.7 ± 0.1 9.9 ± 0.3						
COD a	Whole								
(11,ÅIII)	Filtered	(1) ^c (2)	770 ± 32 -	268 ± 0 -	268		244 ± 127 -	244 ± 127 237 ± 32 	
TSS (mg/L)		(1) (2)	286 281	33 33	31 33		7	6 6 7 7	
VSS (mg/L)		(1) (2)	192 193	5 7	44			· 1	· 1 <1 <1 <1

FIGURES

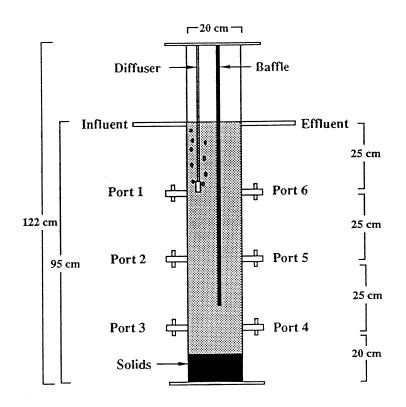


Fig. 1. Aerobic/anaerobic biological reactor.

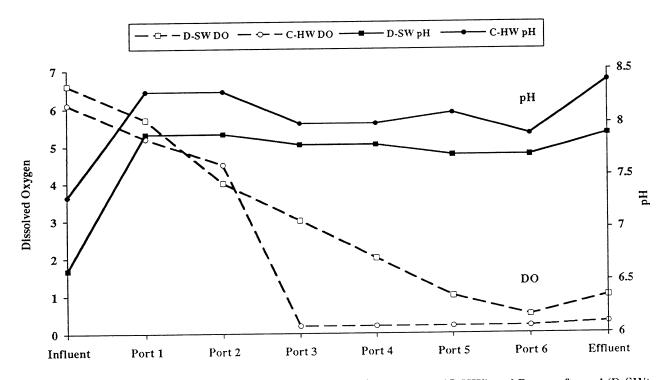


Fig. 2. Dissolved oxygen and pH profiles during sampling of C/D hardwood (C-HW) and D100 softwood (D-SW) wastewaters.

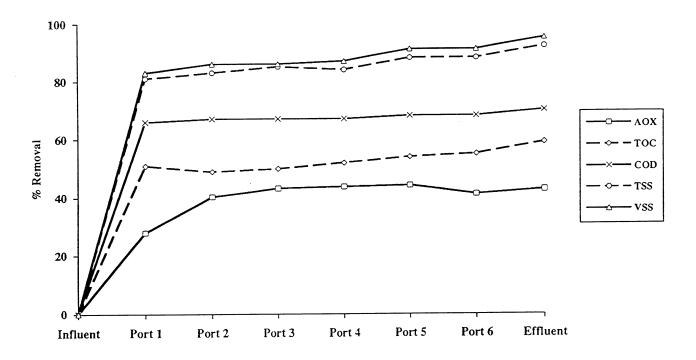


Fig. 3. Percent removal of whole constituents of D100 softwood wastewater throughout biological treatment.

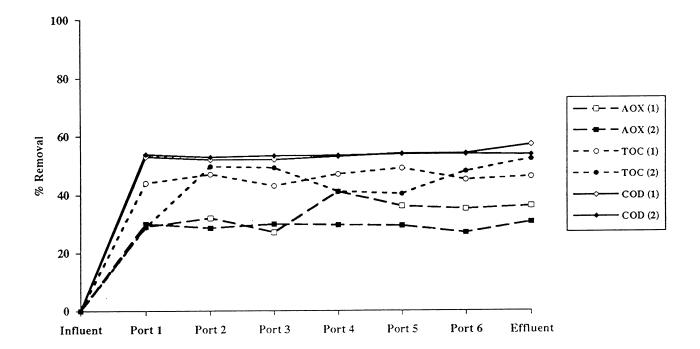


Fig. 4. Percent removal of soluble constituents of D₁₀₀ softwood wastewater throughout biological treatment. (1) and (2) refer to two sample sets taken 8 days apart.

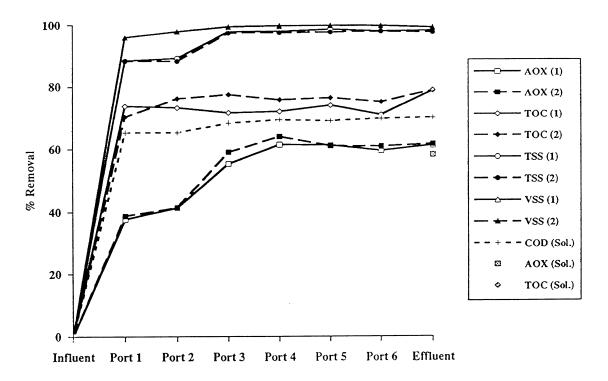


Fig. 5. Percent removal of whole and soluble C/D hardwood wastewater constituents throughout biological treatment. (1) and (2) refer to two sample sets taken 1 day apart; "Sol. " indicates soluble constituents.

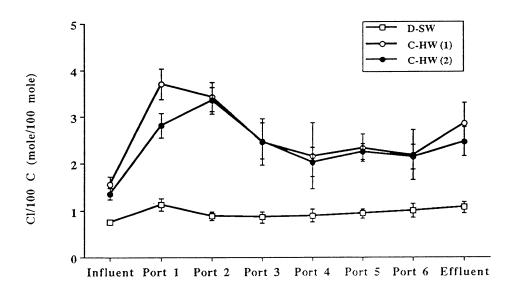


Fig. 6. Chlorine to 100 carbon molar ratios and 95% confidence intervals for whole constituents of D100 softwood (D-SW) and C/D hardwood (C-HW) wastewaters. (1) and (2) refer to two sample sets.

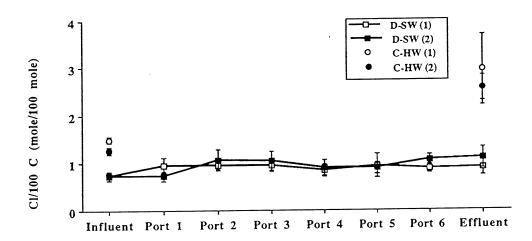


Fig. 7. Chlorine to 100 carbon molar ratios and 95% confidence intervals for soluble constituents of D100 softwood (D-SW) and C/D hardwood (C-HW) wastewaters. (1) and (2) refer to two sample sets.

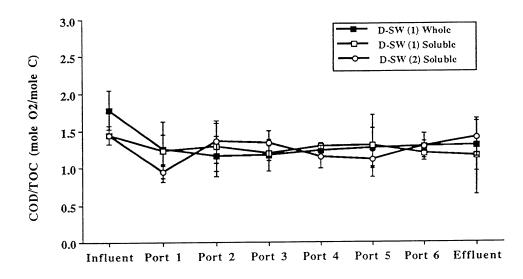


Fig. 8. COD/TOC (O₂/C) molar ratios and 95% confidence intervals of whole and soluble constituents of a D₁₀₀ softwood wastewater.

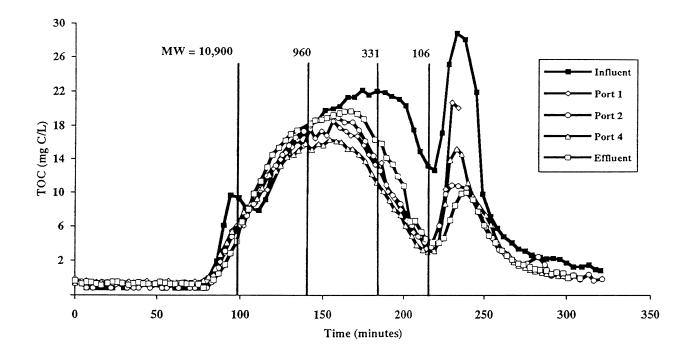
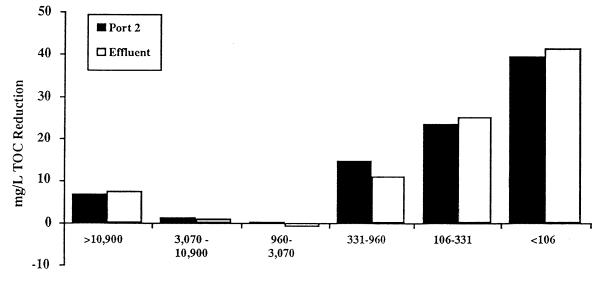


Fig. 9. Gel permeation chromatogram of a D100 softwood wastewater. The lines indicate peak apexes of polyethylene glycol standards.



Molecular Weight Ranges

Fig. 10. Amount of TOC reduced by biological treatment in each molecular weight fraction.