

Treatment of an NSSC effluent in a biological high-efficiency compact reactor

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MILLS THAT PRODUCE NEUTRAL sulfite semichemical pulp (NSSC) are predominantly using hardwood, with pulp yields of 65–85%. Water consumption is low for the NSSC process, so the concentration of organic material is high in the effluent. Carbohydrates, lignin, and wood extractives dominate the content of organic material in pulp and paper mill effluents.

Aspenwood (*Populus*) is one of the highest in extractives content among hardwoods from temperate zones. Acetone extractives of European aspen (*Populus tremula* L.), which reportedly make up 4.5% of the wood, contain large amounts of triglycerides (1). Hardwood NSSC mill effluents have been found to be toxic (2).

For treating pulp and paper mill effluents, it is apparently necessary to use aerobic treatment, either alone or in combination with a preceding anaerobic step (3). Aerobic treatment plants, such as aerated lagoons or activated sludge plants, have long been used to treat various pulp and paper mill effluents. These treatment plants occupy large areas as a result of the need for long hydraulic retention times.

In an activated sludge system with a high-efficiency compact reactor (HCR), the jet loop reactor combines efficient oxygen transfer with turbulent mixing (4). The high-efficiency process utilizes substrates at higher rates than do conventional and modified activated sludge systems. As a result, the high-efficiency

reactors do not need as much land area.

Data have not been reported for the full-scale aerobic treatment of NSSC effluents in a high-efficiency reactor. So far, the efficiency of compact reactor treatments has been reported only for effluents from mills producing mechanical pulps (5–7).

Our aims in this study were to characterize the organic material and their toxicities in the effluent from an NSSC pulping process and to evaluate the efficiency of a full-scale HCR system in removing these materials. We fractionated the mill effluent to determine the phase distribution of the different organic compounds in the effluent. To characterize the total and the fractionated effluent samples, we used the traditional effluent parameters of COD, TOC, and BOD. We also analyzed the main organic constituents, which are carbohydrates, lignin, extractives, and acetates.

MILL AND WASTEWATER TREATMENT PLANT

The mill studied produces 40,000 tons of pulp per year. The mill alternates between aspen and birch as raw material, and it uses sodium sulfite and sodium bisulfate as pulping chemicals. Hydrogen peroxide is used to bleach part of the pulp. During the sampling period, the mill was using European aspen as the raw material, and the pulp was bleached to a brightness of 74–75% ISO, with a pulp yield of 84%.

The biological treatment plant consists of two 250-m³ high-effi-

ABSTRACT

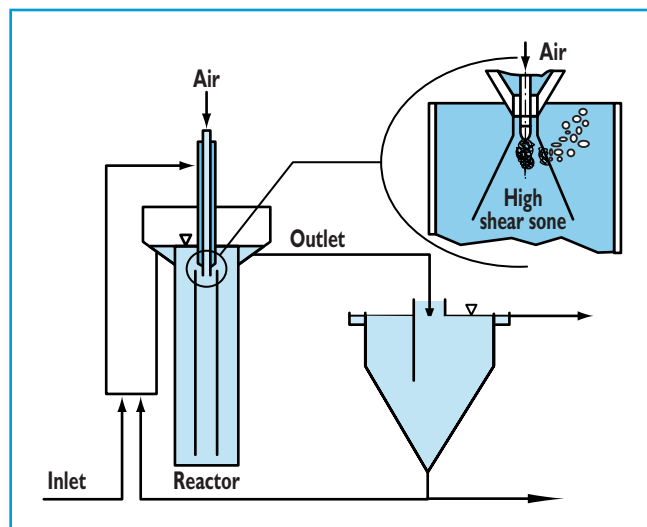
A full-scale, aerobic, compact reactor was used in a biological treatment plant to remove organic material from the effluent of a mill producing aspen pulp in a neutral sulfite semichemical process. The entire biological treatment plant showed high removal efficiencies for the total organic material in the wastewater, removing 65% COD and 93% BOD₅. For filtered samples, the removal rates were 70% COD and 97% BOD₅. The bioreactor removal efficiencies were 99% for identified extractives, 96% for acetates, and 80% for carbohydrates. The removal efficiency for lignin-like material measured by UV absorption was only 15%. The compact treatment system reduced the toxicity of the effluent by 99% and >93% towards the Microtox test bacteria and the *Daphnia magna* water flea, respectively. The main cause of the toxicity was C₁₈-fatty acids.

Application:

In more than 20 installations, high-efficiency compact reactors have performed extremely well with respect to space, time, and yield and in regard to energy requirements. Other advantages are a low sludge volume index and a low production of surplus sludge.

ciency compact reactors in parallel, a flocculation and degassing tank, and a secondary clarifier from Kværner Water Systems. Each of the HCR units has a loop reactor and a special two-phase jet, with the design being derived from the activated sludge process.

As Fig. 1 illustrates, the reactor liquid is pumped into an external loop, where it is mixed with return sludge and untreated mill effluent. The mixture re-enters at the top of the reactor through four nozzles, and



1. Diagram of the high-efficiency compact reactor (HCR).

the pressure drop in the nozzles induces air. The high shear forces created at the outlet of the nozzles produce fine air dispersion and disintegrate the sludge (primary dispersion).

The mixture flows downward through four central tubes. At the upper end of each tube, the jet causes the content of the reactor to circulate in the tubes, resulting in an internal loop flow. The gas bubbles and bacterial flocs in the reactor liquid are thereby re-dispersed (secondary dispersion).

The design load for the treatment system is 35 tons of COD/day, handling a COD feed of up to 17.5 g/L. During sampling, the flow at the inlet was approximately 35 m³/h to each reactor, giving a calculated hydraulic retention time of approximately 7 h. The amount of dissolved oxygen was 1 mg/L, and the amount of suspended solids in the mixed liquor was 9.9 g/L. The temperature was 34°C, and the sludge load was 6.3 kg of COD (filtrated) per kilogram of suspended solids per day.

MATERIALS AND METHODS

Sampling and fractionation

During the winter season (December), samples were collected at the mill outlet, in the reactor loop, and after the secondary clarifier. Each of the main samples was fractionated by centrifugation and membrane filtration.

We centrifuged the samples in 100-mL bottles for 30 min at a relative centrifugal field of 500 g. Both the precipitate and any top-floating layer created were left in the centrifuge tube.

The water phase was pipetted off and labeled as the supernatant, and this supernatant was regarded as containing the colloidal and dissolved substances (8). The supernatant was filtrated through a membrane in a tangential-flow ultrafiltration unit, the "Mini-Ultrasette," (Fil-

tron Technology Corp., USA). The modified polyethersulfone membrane had a molecular weight cut-off of 100,000 Daltons.

The difference between material in the total sample and the material in the supernatant was regarded as the particulate material. The colloidal material was calculated as the difference between the material in the supernatant and that of the membrane filtrate. The dissolved material was calculated as the material in the membrane filtrate.

To study the removal efficiencies for COD and BOD₅, we filtrated the total samples from the mill outlet and secondary clarifier using a Whatman GF/A glass fiber filter.

Chemical analyses

Chemical oxygen demand (COD) was determined photometrically by the closed tube method in a Dr. Lange apparatus (9). Biochemical oxygen demand as BOD₅ and BOD₂₈ and total organic carbon (TOC) were determined at the Norwegian Water Research Institute (NIVA), Oslo, Norway, according to NS 4749 (10), ISO/DIS 9408 (11), and NS/ISO 8245 (12), respectively.

The amount of lignin-like material was determined based on UV₂₈₀ absorption of the remaining water phase after the sample was extracted with methyl *tert*-butylether (MTBE) (13). A mixture of lignans from Norway spruce with an extinction coefficient of 13.9 L/(g·cm) was used as a standard for the quantification.

The carbohydrate content in the water samples was determined by UV₅₄₀ absorption, after acid hydrolysis and the addition of orcinol (3,5-dihydroxytoluene) as a color-complexing reagent (14). A mixture of monosaccharides was used as the standard (5% arabinose, 5% xylose, 55% mannose, 15% galactose, and 20% glucose).

We analyzed the amount of acetate by ion chromatography, using a Dionex 4000 ion chromatography instrument with a conductivity detector. The column was an AS4A-Sc column from Dionex, and 5mM NaBO₂ was used as the mobile phase.

The MTBE-extractable material was analyzed by gas chromatography with a flame ionization detector (GC/FID) with a short, thin-film capillary column (13). The extractions were performed three times at pH 3.5. Heneicosanoic acid, betulinol, and cholesteryl heptadecanoate (Sigma) were used as standards. The extracts were silylated with Tri-sil® (Pierce) before the on-column injection. The extracts were also analyzed on a GC/FID with a long capillary column (15) to quantify the phenols, individual free fatty acids, and extractives in samples with low extractives content.

The phenols, free fatty acids, and sterols were identified by gas chromatography and mass spectrometry (GC/MS). The extractives in the sludge were quantified by GC/MS after extraction of a freeze-dried and hydrolyzed sludge sample (6).

Theoretical COD calculation

We set up COD balances by calculating theoretical COD contributions based on the amount determined for each component group. Each compound's contribution to the theoretical COD was calculated from the measured amount of the organic compound multiplied by its oxygen demand factor (as mg of O₂ per mg of organic compound) (5).

Assuming that oxidation was complete, we calculated the following factors from the compound's molecular formula:

- Carbohydrates - 1.2
- Acetates - 1.1
- Dissolved extractives - 1.6 (phenols)
- Other extractives - 2.8
- Lignin-like material - 1.3.

For the lignin-like material, we used an average molecular formula for lignin sulfonate from hardwood (16).

Toxicity testing

The acute toxicities towards the Microtox bacteria were tested on a Microtox® Model 500 (Microbics Corp., 1991). The 15-min. EC₅₀ values were calculated according to the procedures described in the instrument's manual. Freeze-dried marine luminescent bacteria, *Vibrio fischeri*, were used as test organisms.

To trace the toxic compounds in the effluent, we carried out the Microtox tests on various fractions. Before testing the particulate material from the mill effluent (precipitate and top-floating layer), we re-suspended it in distilled water to the original volume. We evaporated the MTBE-extract from the supernatant under nitrogen to remove the solvent, dissolved it in MeOH, and added distilled water to obtain the original volume.

Methanol was used to increase the solubility of the extractives in pure water. At the concentration used (5% methanol), no toxicity

	Total sample	Effluent phase		
		Particulate phase ^a	Colloidal phase ^b	Dissolved phase ^c
pH	6.4	...	...	...
COD, g/L	14.2	1.0	5.4	7.8
TOC, g/L	4.3	0.1	1.6	2.6
BOD ₅ , g/L	4.7	0.0	0.3	4.4
BOD ₂₈ , g/L	9.2	0.4	4.0	4.8
Lignin-like material, g/L	3.5	0.4	0.5	2.6
Carbohydrates, g/L	3.1	0.1	1.1	2.0
Acetates, g/L	2.5	0.0	0.1	2.4
MTBE extractives, g/L	1.0	0.4	0.5	0.04

^aCalculated as the difference between the material in the total sample and the material in the supernatant.
^bCalculated as the difference between the material in the supernatant and the material in the membrane filter.
^cMeasured in the membrane filtrate.

I. Characteristics of the effluent from the NSSC pulp mill

toward the Microtox bacteria was found, as also reported by Ribo and Kaiser (17). The results are presented here in toxicity units, TU, where TU = 100/EC₅₀ (vol. %). The calculation of EC₅₀ for the toxicants was based on the equation: EC₅₀ (mg/L) = actual conc. of toxicant (in mg/L) ÷ TU.

The acute toxicity towards the water flea *Daphnia magna* was determined by the Norwegian Water Research Institute (NIVA) according to a standardized method (18).

RESULTS AND DISCUSSION

The mill effluent

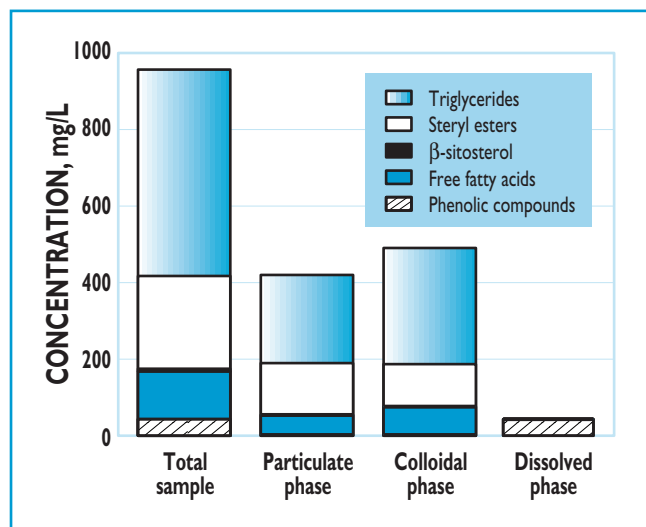
Main characteristics. Table I presents the characteristics of the organic material in the mill effluent. High concentrations of organic material (14.2 g COD/L) were found mainly in the dissolved and colloidal phases. The main part (94%) of the BOD₅ was found in the dissolved phase. This finding shows that the most readily biodegradable organic material was dissolved. As Table I also shows, the effluent had a low content of particulate organic material.

The COD and BOD in the total samples were at the same level or lower than reported for another Nor-

wegian semichemical mill (2). However, these COD and BOD levels were more than three times higher than in effluents from Norwegian integrated newsprint mills (19).

Table I also shows the concentrations of carbohydrates, lignin-like material, MTBE-extractives, and acetates found in the effluent. The lignin-like material was the main compound group and was found primarily in the dissolved phase. More than 75% of the lignin-like material, carbohydrates, and acetates together was found in the dissolved phase. The carbohydrates dominated in the colloidal phase.

As expected, the MTBE-extractable material was found mainly in the particulate and colloidal phases. The extractives were quantified by gas chromatography; the amounts are discussed in more detail below. In addition to the acetate concentration, small amounts of formate and oxalate were also found (16 mg/L of each). The results show low concentrations of lignin-like material and carbohydrates and no acetates in the particulate phase, corresponding to the low COD in this phase.



2. Extractives in the NSSC mill effluent as analyzed by gas chromatography.

To ensure that all major organic compound groups in the wastewater were quantified, we calculated the theoretical COD and compared the calculated values with measured values. The total sample, for the supernatant and the membrane filtrate, gave a total theoretical COD within $\pm 9\%$ of the measured COD. This correlation was equivalent to results obtained in a study of TMP effluent (5), and it shows that all of the main effluent component groups were included in the analytical determinations. Lignin is known to increase the absorption measured in the orcinol method (20), but no correction was made in these calculations for this lignin disturbance in the carbohydrate quantification.

MTBE extractives. The MTBE-extractable material in the effluent included low-molecular-weight lipophilic compounds such as phenols, fatty acids, sterols, steryl esters, and triglycerides. The thin film and short capillary column used in the gas chromatographic analyses enabled us to elute both the small phenolic compounds and the higher-boiling steryl esters and triglycerides in the same run. Extractives in aspen contain high amounts of steryl esters and triglycerides (21–24). In the mill effluent studied, the steryl esters and triglycerides contributed to more than 77% of the total identified extractives and were found in the particulate and colloidal phases (Fig. 2). One fifth of the fatty acids in the mill outlet were found as free fatty acids, and the remaining fatty acids were bound in steryl esters and glycerides.

The most dominant fatty acids in the wastewater were the unsaturated linoleic ($C_{18:II}$) and linolenic ($C_{18:III}$) acids, making up 50% and 40%, respectively, of the total free fatty acids. Palmitic (C_{16}) and stearic (C_{18}) acids constituted the remaining 10%. Fatty acids such as eicosanoic (C_{20}) and docosanoic (C_{22}) acids were also identified, but they were found in negligible amounts.

The same composition of the free fatty acids has

been found in European aspenwood (*Populus tremula* L.) (22). American aspenwood (*Populus tremuloides* Michx.) shows a slightly different composition, with less linolenic acid but more of the saturated acids, including tetracosanoic acid (C_{24}) (21, 23, 24).

In the effluent, the most abundant phenolic compounds identified through gas chromatography were *p*-hydroxybenzoic acid and ferulic acid, or 4-hydroxy, 3-methoxy cinnamic acid. The concentration of *p*-hydroxybenzoic acid was five times higher than for ferulic acid in the total sample. *p*-Hydroxybenzoic acid has been reported as a main component in this type of extractive material and also as a component of the cell wall of aspenwood (25, 26). Ferulic acid has been found in European aspen but not in its American relative (26).

Because they are highly soluble in water, these phenols dominated the extractives in the membrane filtrate. As expected, the dissolved phase had low concentrations of fatty acids and sterols but no steryl esters or triglycerides. The steryl esters and triglycerides are too hydrophobic for dissolution in the water phase.

Of the sterols and triterpene alcohols, β -sitosterol was found to be dominant. Other compounds identified were β -sitostanol, β -lanosterol, amyrin, cycloartenol, lupeol, stigmast 4-en 3-one, and 24-methylenecycloartenol. Except for β -lanosterol, these compounds have previously been found in both *Populus tremula* L. and *Populus tremuloides* Michx. (27, 28). β -lanosterol was identified only from the GC/MS library.

Acute toxicity. The untreated NSSC mill effluent was tested for acute toxicity towards the Microtox® bacteria *Vibrio fischeri* and the water flea *Daphnia magna*. The effluent was highly toxic for the Microtox bacteria, as Table II shows. The material in the colloidal and particulate phases was responsible for most of this toxicity, as indicated by the low toxicity found in the dissolved phase. Previously, Broch-Due *et al.* found similar toxicity for an NSSC effluent toward the Microtox bacteria (2).

For the total sample, the acute toxicity towards the bacteria was significantly different from the toxicity toward the water flea *Daphnia magna*. However, the discrepancy is in accordance with previous findings of effluent testing in pulp and paper mills (29, 30). This difference in sensitivity is probably caused by differences both in the test species and in the test conditions. Different species used in laboratory experiments respond differently to effluents, which means that more than one species should be used in evaluating toxicity (31).

Differences in sensitivity have also been explained by differences in pH in the test samples. A reduction in pH from 8 to 7 has been shown to increase the toxicity for resin acids (32, 33). The Microtox test is carried out at neutral pH, whereas the testing for water fleas is carried

out at pH 8. At higher pH, more of the extractive acids are dissociated, giving higher water solubility and reduced bioavailability.

The results from the Microtox testing are given in toxicity units (TU) in Fig. 3. The sums of the measured toxicity units for the fractions were shown to be within $\pm 5\%$ of the measured TU for the total sample (136 + 417) and for the supernatant (180 + 255). The results indicate absence of both synergetic and antagonistic toxicity effects of the separated compounds.

The lipophilic MTBE extractives were found to be partly responsible for the toxicity in mill effluent (55%) and were detected mainly in the particulate and the colloidal phases (Fig. 2). The distribution of the extractives between the particulate phase (44%) and the colloidal phase (56%) corresponded to the toxicity distribution found for the same phases in the supernatant (43% in the re-suspended particulate material and 57% in the re-dissolved MTBE extractives).

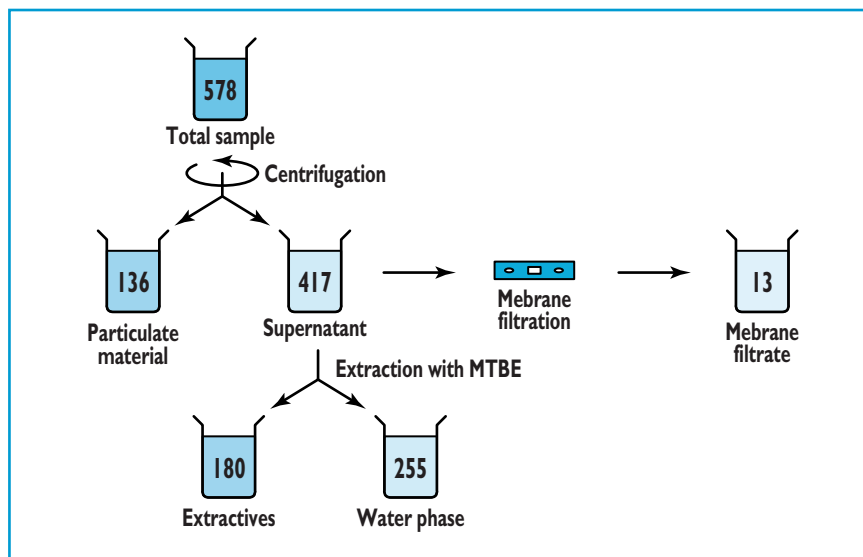
Extractives such as resin acids, juvabionones, and free C_{18} -fatty acids, instead of the total extractive material, are thought to be the main cause of the toxicity (29, 34). The effluent studied contained no resin acids or juvabionones, so the free fatty acids were assumed to contribute all the toxicity from the lipophilic extractives.

The free C_{18} -fatty acids showed the same phase distribution in the effluent as did the total extractives. Calculation of EC_{50} for the C_{18} -fatty acids gave an EC_{50} of 0.4 mg/L for the acids in both the particulate material and in the extractives from the supernatant, showing good agreement with previously reported Microtox results (35). The results showed that the toxicity testing of the fractions was useful for tracing the most important toxicants in the wastewater.

	Microtox ^a		Daphnia magna ^b	
	EC_{50} , % by vol.	95% conf. interval	EC_{50} , % by vol.	95% conf. interval
Total sample	0.17	(0.13–0.23)	3.5	(1.7–11)
Supernatant	0.24	(0.15–0.39)	2.8	(2.5–3.2)
Membrane filtrate	7.60	(6.50–8.80)	7.0	(6.3–7.7)

^aMicrotox treatment = 15 min. ^bTreatment with *Daphnia magna* = 48 h.

II. Toxicity data for the untreated mill effluent



3. Fractionation scheme for the toxicity testing. The results are given in toxicity units on the tubes. (The particulate material was re-suspended before testing, and the extractives were re-dissolved in 5% methanol in water.)

In the water phase after extraction with MTBE, the toxicity was still high (255 TU). The cause of this toxicity has not been identified. However, because the toxicity in the membrane filtrate was low, we expect that this high TU value was caused by compounds of high molecular weight or by nonextractable compounds associated with colloidal material. Further toxicity fractionation studies of the water phase are needed for identifying the toxic compounds in this phase.

The low toxicity in the membrane filtrate (13 TU) may be caused partly by the dissolved extractives. Calculated TU values for *p*-hydroxybenzoic acid and C_{18} -fatty acids account for half the measured toxicity (3 TU and 4 TU, respectively). We

calculated the TU values using an EC_{50} value for *p*-hydroxybenzoic acid of 11.75 mg/L (36) and using the value calculated earlier for the free C_{18} -fatty acids.

Biological treatment

Reduction of organic material in the treatment plant. Efficiencies over the entire treatment plant are presented in Table III. Common wastewater parameters were measured first at the mill outlet and then at the outlet from the secondary clarifier, and the differences in values were used to determine the removal efficiencies.

The removal efficiencies found were higher than those reported for a conventional activated-sludge pilot plant treating NSSC/CTMP effluent that had only one fourth of the COD

	Removal, %	
	Total plant	HCR
COD		
Total sample	65	...
Filtrated sample*	70	...
Supernatant	...	59
BOD ₅		
Total sample	93	...
Filtrated sample*	97	...
Supernatant	...	84
BOD ₂₈		
Supernatant	...	81
TOC		
Supernatant	...	63
Supernatant material		
Lignin-like material	...	15
Carbohydrates	...	80
Acetates	...	94
MTBE-extractables	...	99

*Filtrated with a Whatman GF/A glass fiber filter.

III. Removal efficiencies for the organic material in the treatment plant

concentration in the effluent used in our study (3). A pilot plant with a moving-bed bioreactor, which was also treating NSSC effluent, showed higher removal efficiencies than the efficiencies of our study, with removal rates of 75–80% for soluble COD (2). Comparisons like these do not always properly reflect the treatment efficiencies of different plants however, because of differences in the effluents treated. Generally, NSSC effluents are more difficult to treat biologically than are the effluents of other types of processes, such as thermomechanical pulping.

To study the reduction of components, we compared centrifuged samples from the mill outlet with centrifuged samples from the reactor loop (Fig. 1). The results reflect the removals in the reactor at the short retention time, being unaffected by further removal in the degassing-flocculation tank and the secondary clarifier. The bioreactor removal effi-

ciencies for the different groups of organic compounds are shown in Table III. Because the samples were centrifuged, the results are independent of the proclivity of the sludge to settle, and the results presented show the removal efficiencies of the colloidal and dissolved material.

The bioreactor removal efficiencies for COD and BOD₅ were somewhat lower than those found for the filtrated samples measured over the total treatment plant. The reduction efficiency for BOD₂₈ was nearly as high as for BOD₅, although the BOD₂₈ concentration in the untreated mill effluent was almost twice as high as the BOD₅. The difference between BOD₂₈ and BOD₅ was mainly due to differences in the colloidal material, as Table I shows. For the more resistant part of the biodegradable organic material, the removal mechanism may be either biodegradation in the reactor or adsorption to the sludge (5).

Of the groups of organic compounds analyzed, the extractives and acetates had the highest removal efficiencies in the bioreactor. There seems to be a potential for further removal of the carbohydrates in the bioreactor, since these compounds normally are readily biodegradable. About a third of the carbohydrates were found in the colloidal phase before the biotreatment, as Table I shows. These carbohydrates may be of high molecular weight or may be bound to colloidal material (e.g., cross-linked by lignin), with either condition being prone to reduce biodegradation (37).

The lignin-like material was reduced by only 15% in the bioreactor, and this partial reduction was the main reason that complete COD removal was not attained. Not only do particulate organic materials adsorb to activated sludge, but soluble organic substances do as well (38). However, the lignin-like material had low adsorption to the sludge,

as indicated by its low removal efficiency in the bioreactor. Sulfonation, which increases the water solubility of the lignin, can be the reason for both the low adsorption and the low biodegradation of the lignin-like material. The lignin-like material in the supernatant shows the same reduction both by biotreatment and membrane filtration. However, the material removed may still be from different fractions of the measured lignin-like material—i.e., fractions of material with different molecular weights.

Low reduction efficiencies for lignin compounds have been found for activated sludge treatment of CTMP effluent (39). The highest removal efficiencies for lignosulfonates has been reported by Liu *et al.* (40). In their work, as much as 55% of the lignosulfonates was removed during laboratory activated-sludge treatment of the effluent from a CTMP process pulping 90% black spruce and 10% eastern hemlock. They also reported low adsorption of lignosulfonates on the sludge.

In the centrifuged sample from the reactor loop, the group of lignin-like materials was the main constituent, contributing about 80% of the residual COD. Escaping the aerobic biological treatment, this material is expected to be poorly biodegradable in the receiving environment.

Residual extractives after the biotreatment. Low concentrations of extractives were found in the sample taken from the reactor loop, as Table IV shows. Small amounts of *p*-hydroxybenzoic acid were found in both the colloidal and dissolved phases, while ferulic acid could not be detected. The concentration of the fatty acids in the dissolved phase of the reactor loop was equal to the concentration found in the same phase of the untreated mill effluent. This finding most likely shows the solubility of the acids at the current pH and salinity conditions (41, 42).

	Colloidal phase, mg/L		Dissolved phase, mg/L	
Phenolic compounds				
p-Hydroxybenzoic acid	1.0		0.6	
Ferulic acid	n.d.		n.d.	
Sum	1.0	= 1.0	0.6	= 0.6
Fatty acids				
Free fatty acids				
Palmitic acid	0.5		0.7	
C ₁₈ -fatty acids	1.4		1.7	
Bound fatty acids				
Palmitic acid	0.2		n.d.	
C ₁₈ -fatty acids	2.2		n.d.	
Sum	4.2	= 4.2	2.4	= 2.4
Sterols				
Free β-sitosterol	0.3		traces	
Bound β-sitosterol	0.1		...	
Sum	0.4	= 0.4	traces	= 0.0
Total identified extractives		5.6		3.0

n.d. = not detected.

IV. Extractives found in the treated wastewater taken in the reactor loop.

The C₁₈-fatty acids in the two membrane filtrates had slightly different compositions. In the sample from the reactor loop, we found more oleic acid. The difference is probably caused by the production of fatty acids by the bacteria in the reactor, which would affect the fatty acid composition. Liu *et al.* previously observed slightly lower removal efficiency for oleic acid than for linoleic acids (40).

Of the free sterols, β-sitosterol was removed by 97%. This percentage is a higher removal efficiency than has been reported for other aerobic treatments of pulp and paper mill effluents (43, 44).

Biosorption of extractives. In a sludge sample from the reactor loop analyzed for extractives by gas chromatography, we found 2.4 mg of palmitic acid per gram of dry sludge and 9.7 mg of C₁₈-fatty acids per gram of dry sludge. The C₁₈-fatty acid composition on the sludge was similar to that found in the supernatant from the reactor loop.

Of the sterols, 0.7 mg of β-sitosterol per gram of dry sludge was quantified. Other sterols and triterpene alcohols we identified showed patterns similar to that found in the mill effluent. No *p*-hydroxybenzoic or ferulic acids were detected.

Toxicity reduction in the reactor. The acute toxicity measured toward the Microtox bacteria and the water flea *Daphnia magna* showed reductions of 99% and >93%, respectively, as a result of the bioreactor treatment. Table V presents the results. The same high level of toxicity reduction has been found for NSSC effluent treated in a moving-bed bioreactor in a pilot plant (2).

The toxicity reduction in the supernatant was similar to the reduction of the extractive material. The low toxicity in the biotreated wastewater also indicates the removal of the toxic material in the water phase.

SUMMARY

The NSSC mill effluent based on European aspen showed high con-

	EC ₅₀ , vol. %	
	Microtox ^a	<i>Daphnia magna</i> ^b
Reactor loop		
Supernatant	21.8	>40
Filtrate	79.0	>63
Tox. removal, %	99	>93

^aMicrotox treatment = 15 min.
^bTreatment with *Daphnia magna* = 48 h.
The 95% confidence intervals were: 20.0-23.8 for the supernatant and 56.6-110.3 for the filtrate.

V. Toxicities of the wastewater after biological treatment and the toxicity removals in the reactor

centrations of organic material, with 14.2 g COD/L. The main part (94%) of the most readily biodegradable organic material, measured as BOD₅, was found in the membrane filtrate. The fatty acids were linoleic and linolenic acids, contributing 90% of the total free fatty acids. One fifth of the fatty acids were found as free acids, and the rest were bound as triglycerides and steryl esters. *p*-Hydroxybenzoic and ferulic acids were identified as the main dissolved extractives.

In the untreated effluent tested, toxicity fractionation showed that extractives contributed 55% of the toxicity towards the Microtox bacteria. EC₅₀ (15 min) for C₁₈-fatty acids in the untreated mill effluent was calculated to be 0.4 mg/L. The Microtox test was found to be more sensitive than the *Daphnia magna* test for the particulate and colloidal material in the mill effluent. This discrepancy was caused by differences in the test species and in the test conditions (pH).

The biological treatment plant showed high removal efficiencies for the total organic material in the NSSC mill effluent, removing 65% COD and 93% BOD₅. The corresponding removals for filtered samples were 70% and 97% respectively. The bioreactor removal efficiencies at a short retention time (7 h) were 99% for the identified extractives, 96% for the acetates, and 80% for the

carbohydrates. The lignin-like material measured by UV absorption was reduced by only 15% in the bioreactor. The acute toxicities measured towards the Microtox bacteria and *Daphnia magna* were both reduced by more than 93%. **TJ**

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