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REMOVAL OF ORGANIC AND TOXIC SUBSTANCES FROM DEBARKING AND KRAFT PULP BLEACHING EFFLUENTS BY ACTIVATED SLUDGE TREATMENT

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Pilot plant experiments were carried out in a Finnish kraft mill to test the treatment of combined debarking and bleaching effluent by the activated sludge method. The best BOD_7-reduction obtained was 60-80 %. Resin acids, an important group of toxic compounds, were reduced efficiently, the average reduction being 75 %. The reduction of chlorinated phenolics was usually 30—40 %, and at best about 60 %. Acute toxicity (LC-50 96 h) to trout was reduced by at least 70 %. Long term toxicity tests (20 d) revealed that the treatment reduced sublethal effects and the accumulation of resin acids in trout. Compounds tainting fish fillets were also reduced.

Index words: Debarking effluents, kraft pulp bleaching effluents, activated sludge treatment, toxicity, fish test, rainbow trout, resin acids, chlorinated phenolics, organoleptic analyses.

1. INTRODUCTION

Bleaching is presently the most important source of pollution in pulp mill processes in Finland. Many other processes in the pulp and paper industry, such as washing and grading, have been converted almost completely to closed water circulation and therefore the relative significance of bleaching effluents has increased. In Finnish pulp mills 30-50 % of BOD_7, over 70 % of COD, about 80 % of colour and a considerable part of toxic compunds come from bleaching. The proportion of debarking effluents in the waste water is usually also considerable.

Some experiments using completely closed bleaching water circulation have been carried out in other countries (Kramer et al. 1979). Also, a number of methods have been developed for the purification of bleaching effluents (Gove 1979). However, to date there is little knowledge available concerning the application of these methods in Finnish conditions.

The National Board of Waters in Finland, in cooperation with Kokkola Water District and the company Oy Wilh. Schauman Ab, has carried out experiments on the purification of bleaching and debarking effluents in a kraft mill at Pietarsaari, a town located on the coast of the Gulf of

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Bothnia. In 1978 pilot scale experiments were carried out on the treatment of alkaline effluent of bleaching by activated sludge and biofiltering methods. The reduction of organic matter in undisturbed circumstances was found to be satisfactory. However, it was very difficult to operate the process because of great variations in the quality of alkaline waste water. In the following year acidic effluent of bleaching and clarified effluent of debarking were also included in the purification experiments, with the aim of reducing the variations in effluent quality. The purpose was also to satisfy part of the nutrient demand of the biological purification process by nutrients in the debarking effluent. The experiments were carried out using the activated sludge process.

2. QUALITY OF THE WASTE WATER

The effluent investigated consisted of acidic and alkaline bleaching effluents and debarking effluent from primary sedimentation. The kraft mill used a typical multistage chlorine bleaching method (C/D EDED). Conventional wet debarking drums were used for debarking. Effluent fractions were taken into the pilot plant in the same proportions in which they originated from the mill processes, i.e.:

- alkaline bleaching effluent 12 %
- acidic bleaching effluent 32 %
- clarified debarking effluent 56 %

Alkaline bleaching effluent has very high colour values, especially when softwood is used as the raw material. This is caused by complex lignin compounds, which are not easily degradable. The molecular size of lignin compounds from the chlorine and dichlorine stages of bleaching is small and the compounds are therefore easily degradable. Bleaching effluent contains hardly any nutrients (P and N). The most harmful toxic compounds are chlorophenols.

The organic matter of debarking effluent is fairly easily degradable. In addition, this effluent contains considerably more nutrients than bleaching effluent. Table 1 presents quality of the combined effluent after neutralization.

The colour of effluent depended very much on the wood raw material. When softwood was used as raw material the average colour of the combined waste water was about 3 g l^{-1} Pt but when hardwood was used the colour was only 1.8 g l^{-1} Pt.

Table 1. The average quality of untreated effluent

Parameter		Average	Standard deviation	Number of observations
SS	mg l^{-1}	189 ± 115		81
BOD_7	mg l^{-1} O_2	257 ± 75		80
COD_{Cr}	mg l^{-1}	1005 ± 374		77
TOD	mg l^{-1} O_2	751 ± 230		29
TOC	mg l^{-1} O_2	308 ± 83		32
P	mg l^{-1}	1,09 ±0,54		49
N	mg l^{-1}	3,09 ±1,49		48
Colour	mg l^{-1} Pt	2460 ±1698		74

Table 2. Experimental periods

Period	Date (1979)	Dosage of aluminium-sulphate mg l^{-1}	Dosage of ferrous sulphate mg l^{-1}	Dosage of nutrients
I	9.7.– 3.9.	-	-	-
II	4.9.– 24.9.	100-450	-	-
III	25.9.–29.10.	-	-	+
IV	30.10.–5.11.	-	100	+
V	6.11.–12.11.	100	-	+

3. EXPERIMENTAL

3.1 Pilot plant equipment

The tests were run with a normal one-stage activated sludge system. The volume of the aeration basin of the pilot plant was 11 m^3. The equipment included a pH-regulator, dosing pumps for chemicals, effluent sampling and measuring devices and an exchanger for reducing the temperature of the incoming effluent. The flow sheet of the pilot plant is illustrated in Fig. 1.

3.2 Experimental periods

Pilot plant experiments were carried out during the period 9.7.1979–12.11.1979 (Table 2).

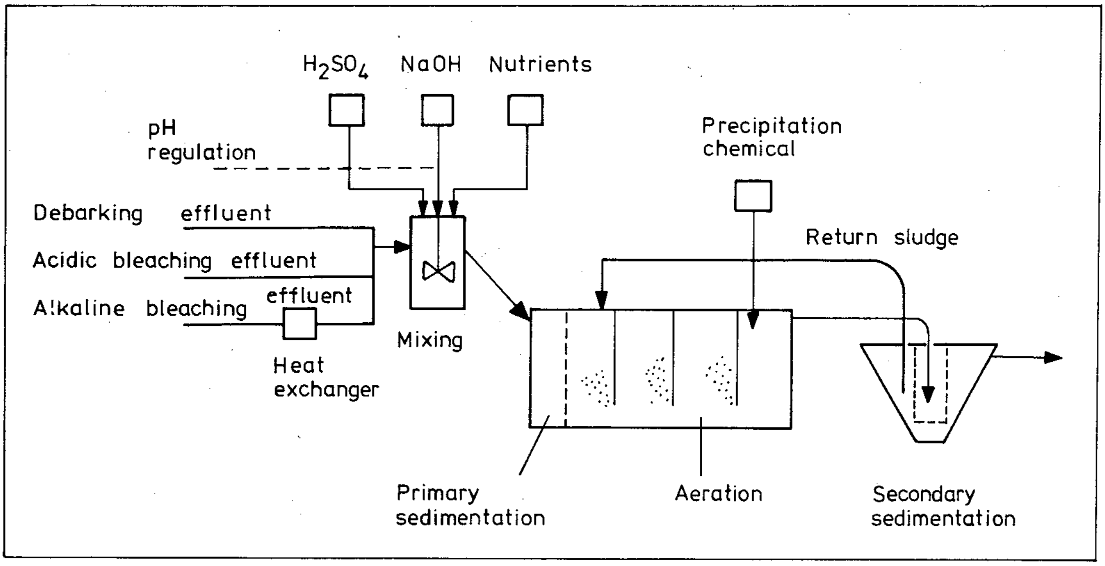

Fig. 1. Flow sheet of the pilot plant.

The organic load of the pilot plant was about 1 kg m^{-3} BOD_7. The sludge concentration in the aeration basin varied between 1 and 7 kg m^{-3}. The average sludge load was 0.25 kg BOD_7/kg MLSS·d and it varied as shown in Fig. 2. The temperature of the activated sludge was over 20°C almost throughout the whole experimental period. In summer, when the temperature threatened to increase over 30°C, the alkaline waste water of bleaching was lead through the heat exchanger.

Without addition of nutrients the relation BOD_7: N:P was on average 100:0.94:0.33. The purpose of addition of nutrients was to change this relation to 100:4:1. Diammonium phosphate and urea were used as the nutrient solution. The pH of the incoming combined effluent was 4–5 and was neutralized to pH 6.5–7.5.

3.3 Analytical methods

In this work the analyses of toxic compounds were based on their ether extractions. The system used to analyze toxicants is shown in Fig. 4 (Holmbom 1980).

4. RESULTS AND DISCUSSION

4.1 Removal of organic substances and nutrients

During undisturbed periods of operation the BOD_7-reduction was 60-80 % even without addition of nutrients. Because of operational problems during the experimental periods, sludge from the municipal treatment plant had to be added, which propably influenced the results. After mid-October the purification effect began to worsen, although no operation problems occurred and for example settling properties were good. The reason for this was propably a strong drop in temperature and its effect on micro-organisms. Poor purification results were also observed during the second experimental period, when aluminium sulphate was added in order to remove colour. The sludge began to settle very poorly, which caused the poor results. Figure 3 shows the BOD_7 values of the effluent before and after treatment.

When the external purification of kraft mill effluent is considered, one principle is that the nutrient load should not increase. Usually this is the case if nutrients are added to the activated sludge process and if post precipitation is not used.

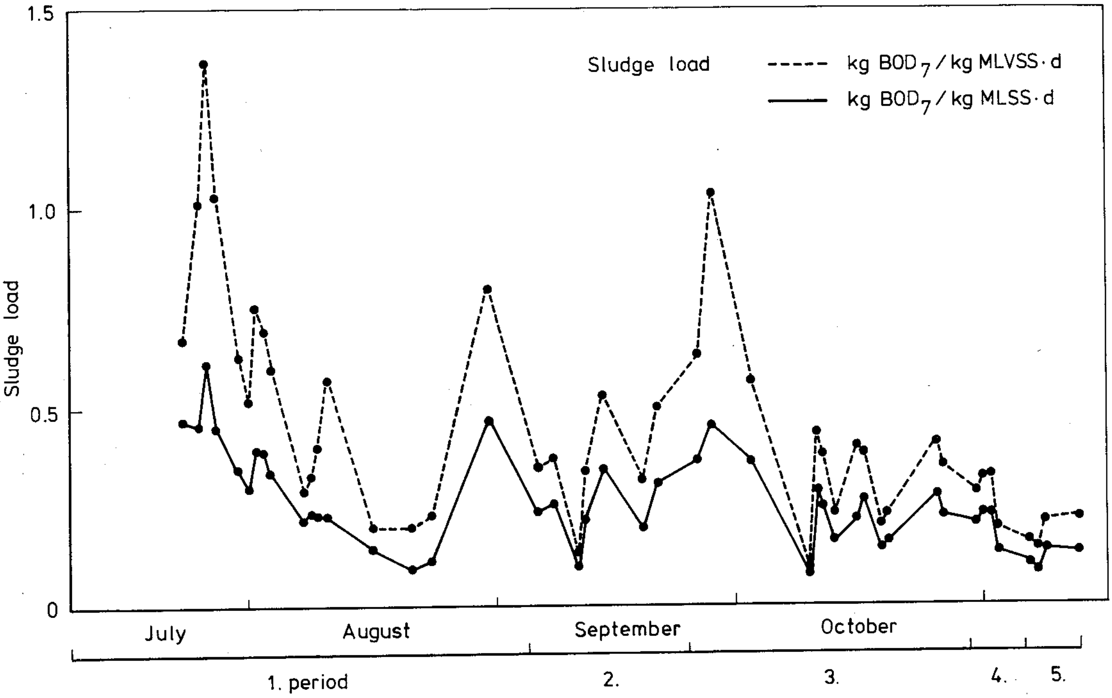

Fig. 2. Variation of sludge load during pilot plant runs.

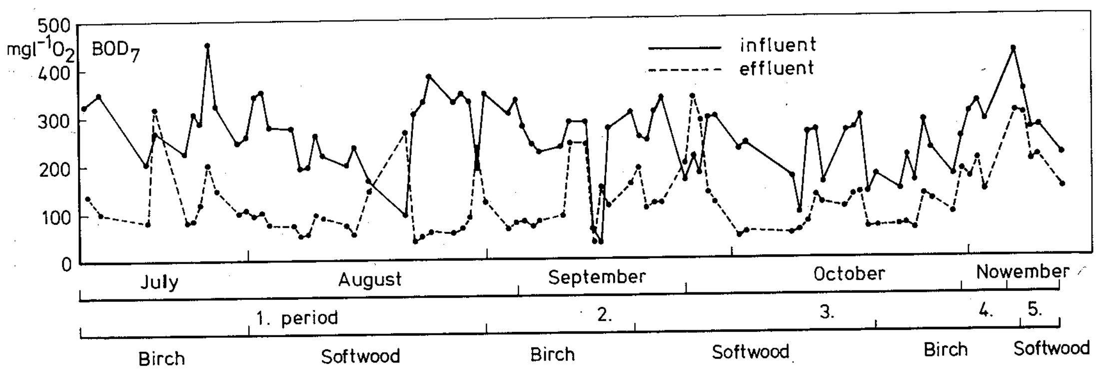

Fig. 3. BOD_7 values before and after treatment.

Because of nutrient dosage the phosphorus concentration increased in treated effluent by about 1–2 mg l^{-1} during periods 3–5. The purification process itself had only small effect to the average phosphorus content.

One of the original objectives was to try to precipitate excess phosphorus simultaneously with aluminium sulphate and ferrous sulphate. Unfortunately this part of the experiment was too short, due to construction work in the mill area at the same time.

An effort was made to remove colour by adding aluminium sulphate to the aeration basin. The dosages were chosen after laboratory tests so that the feed was increased by small increments from 100 mg l^{-1} to 450 mg l^{-1}. The

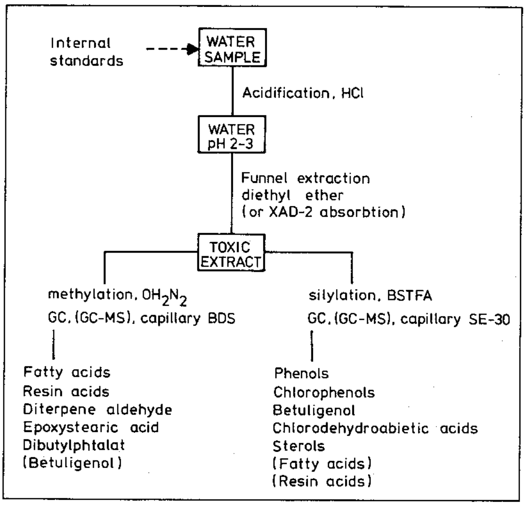

Fig. 4. Scheme for analysis of toxic compounds in pulp and paper mill effluents.

results were poor because the settling properties of the sludge were deteriorated considerably. Thus reliable conclusions concerning the other parameters of this period cannot be drawn.

4.2 Removal of toxic substances

A common opinion is that lipophilic compounds and toxicity of waste water are strongly correlated. Lipophilic compounds can enrich in the fatty tissue of an organism. As much as 75-92 percent of the toxic compounds of bleaching effluents are ethersoluble (Sameshina et al. 1979).

The toxic and other compounds of different effluent streams are shown in Table 3.

4.21 Total ether extraction content

Ether-soluble compounds give a rough estimate of the total amount of toxic substances. Using the activated sludge method 51 %, on average, of ether-soluble substances could be removed from the combined effluent.

4.22 Resin acids

Resin acids orginate mainly from softwoods and here they occurred mostly in debarking effluent. Table 4 shows resin acid concentrations before treatment (combined effluent), respective reductions and toxicity values. Other identified resin acids were sandarakopimaric, dehydrodehydroabietic and dihydroabietic acid.

It can be concluded that the activated sludge method is very efficient in removing resin acids. The concentration of dehydroabietic acid was the highest of the resin acids and therefore the most important from the point of view of toxicity. Its reduction was about 80 % on average. A similar reduction efficiency of total effluent and different resin acids has been reported by Easty et al. 1978. The content of neoabietic acid, which has been reported to

Table 3. Contents of toxic and other compounds in untreated effluents

Compound	Debarking effluent $\mu g\,l^{-1}$	Bleaching effluents Acidic $\mu g\,l^{-1}$	Bleaching effluents Alkaline $\mu g\,l^{-1}$	Combined effluent 1) $\mu g\,l^{-1}$	Foam 1) $\mu g\,l^{-1}$
Resin acids	6 600	170	390	2 600	1 550
Chlorinated phenolics	-	520	1 270	180	220
Saturated fatty acids	1 500	420	7 600	1 680	4 800
Unsaturated fatty acids	600	30	320	+	1 050
9,10-epoxystearic	-	-	350	400	-
Betuligenol	780	+	60	880	160
Sitosterol	200	+	40	70	170
Betulinol	370	400	2 000	1 080	700
Total ether-soluble compounds 2)	50 600 2)	45 600 2)	184 600 2)	46 800 3)	-

1) Sampling date not identical to other effluent streams
2) Gravimetric analyses
3) Calculated value of 11 double samples

Table 4. Resin acid contents before treatment and their respective reductions (excluding values obtained during operational disturbances) and LC-50 values to fish according to Leach and Thakore (1976)

Resin acid	Content before treatment mg l^{-1}		Reduction	LC-50
	Average	Maximum	%	mg l^{-1}
Dehydroabietic	1.24	3.78	81	1.1
Abietic	0.49	1.23	75	0.7
Neoabietic	0.25	0.66	74	
Palustric	0.13	0.43	63	0.5
Pimaric	0.28	0.59	72	0.8
Isopimaric	0.30	0.58	77	0.4
Others resin acids	0.15	0.25		
Total	2.84	7.24	79	1.0

Table 5. Identified chlorinated phenolics, their concentrations, reductions by the activated sludge method and LC-50 values to fish according to Leach and Thakore (1975), Salkinoja-Salonen et al. (1981), Voss et al. (1981) and Servizi et al. (1968).

Chlorinated phenolics	Average content $\mu g\ l^{-1}$		Reduction	LC 50
	in	out	%	mg l^{-1}
a) 2,4,6-trichlorophenol	34	19	45	2.2
b) 4,5-dichloroquaiacol	25	14	42	4.8
c) Isomer of b)	25	15	39	
d) 3,4,5-trichloroquaiacol	+	+	30	0.75
e) Isomer of d)	55	45	18	
f) 3,4,5,6-tetrachloroquaiacol	12	12	0	0.32
g) 3,4-dichlorocatechol	+	+	58	2.7
h) Isomer of g)	28	45	59	
i) Isomer of g)	16	+	56	
j) 3,4,5-trichlorocatechol	67	42	37	0.89
k) Tetrachlorocatechol	20	+	72	0.40
l) 2,6-dimethoxy-3,4,5-trichlorophenol	29	12	57	3.4
Total chlorinated phenolics	328	226	31	

be mutagenic for bacteria (Nestmann et al. 1979), was about 0.25 mg l^{-1} in the influent. Its reduction was about 74 %. The reduction of resin acids was usually good when the pilot plant was operating without disturbances. Usually when BOD_7-reduction was good resin acid reduction was also good (Fig. 5).

4.23 Chlorinated phenolics

Another important group of toxic compounds is chlorinated phenolics, which are born in the bleaching process when chlorine and chlorine dioxide react with lignins. It is not well known how chlorinated phenolics behave in biological purification processes. However experiences presented by Hakulinen and Salkinoja-Salonen (1981) show that reduction achieved by conventional biological methods is usually below 30 %. Table 5 presents the average contents of

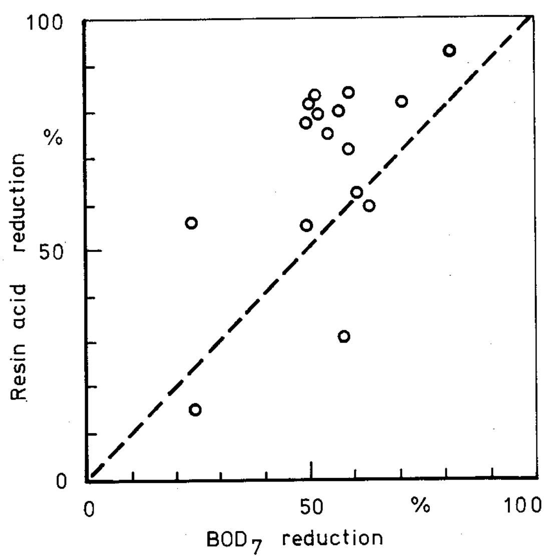

Fig. 5. Dependence of resin acid reduction on BOD_7 reduction. Values during undisturbed runs are only included.

Table 6. Concentrations and reductions of different fatty acids.

Fatty acid		Average content ($\mu g\,l^{-1}$) in	out	Reduction %
Palmitic acid	(16 : 0)	500	230	54
Stearic acid	(18 : 0)	290	170	41
Arachidic acid	(20 : 0)	270	100	63
Behenic acid	(22 : 0)	370	180	51
Lignoceric acid	(24 : 0)	130	60	54
Total saturated		1560	740	53
Oleic acid	(18 : 1)	<30	<30	–
Linoleic acid	(18 : 2)	<30	<30	–
Total unsaturated		<60	<60	–

identified chlorinated phenolics, their reductions and LC-50 values. The overall average reduction of chlorinated phenolics was here also about 30 %.

4.24 Fatty acids and other compounds

Most of the fatty acids were saturated, which means that every molecule contained 16, 18, 20, 22 or 24 carbon atoms (symbols correspondingly 16 : 0, 18 : 0, 20 : 0, 22 : 0 and 24 : 0). The origin of unsaturated fatty acids is mainly debarking effluent, although they also occur in low concenstrations in the alkaline extraction of bleaching effluent. Identified unsaturated fatty acids were oleic acid (18 : 1) and linoleic acid (18 : 2). Saturated fatty acids are not very toxic (LC-50 >20 mg l^{-1}, while unsaturated fatty acids are more toxic (LC-50 8–9 mg l^{-1}). Table 6 shows the concentrations of fatty acids and their reductions in the pilot unit.

9.10-Epoxystearic acid is a very toxic compound (LC-50 1.5 mg l^{-1}. Leach and Thakore, 1975) which comes from the alkaline stage of bleaching. Its reduction in the pilot plant was 70-80 % (Table 7). The source of betuligenol and ketobetuligenol was birch bark. No information is available in the literature concerning their toxicity. Their reductions in the pilot plant were good (75-85 %, Table 7).

Sterols occurred in all effluent streams, but mostly in debarking effluents. In combined untreated effluent their content was about as high as that of total saturated fatty acids (Table 7). The content of betulinol, a compound of birch wood, was about half that of sterols. No indication of the toxicity of sterols is given in the literature, because it is thought that their toxicity is negligible. Reduction of sterols in the pilot plant was 50-55 %.

Table 7. Contents of sterols and some other compounds and their reductions during treatment.

Compound	Average content($\mu g\,l^{-1}$) in	out	Reduction %
Betulinol	1 660	620	63
β-sitosterol	250	150	40
β-sitostanol	110	50	55
Lupeol	130	60	55
Other sterols	220	200	9
Total sterols	2 370	1 080	54
9,10-Epoxystearic acid	500	130	74
Betuligenol	800	140	82
Ketobetuligenol	270	70	74
Pimaral	80	30	62
Dibutylphtalate	< 30	< 30	–
Squalene	110	–	–
Guaiacol	45	< 30	–

Other easily identified compounds and their reductions are shown in Table 7. According to chromatographs there were still many unidentified compounds in the combined waste water. However, no further studies were carried out.

5. EFFICIENCY OF TREATMENT EVALUATED BY BIOTESTS WITH FISH

Pulp mill effluents contain many compounds toxic to aquatic life. Because of the combined effects of any complex effluent a biotest is the only reliable means of assessing toxicity (Chung et al. 1979). The biotest is thus a quantitative measure of the integrated effect of the toxic factors in the effluent.

This part of the study deals with the effects of biological treatment on the toxicity of the debarking and bleaching effluents to fish (Miettinen et al. 1982). LC-50-tests were carried out to evaluate the overall short-term toxicity. Long-term testing with sublethal concentrations was used to evaluate the effects of effluent on the physiology and organoleptic properties of fish. Furthermore, reduction of resin acids in the treatment was estimated by analysing the accumulation of these compounds in the blood plasma and bile of fish.

5.1 Material and methods

The fish used in the tests were rainbow trout (Salmo gairdneri), 0 + year old in the LC-50 (96 h) tests and 1+year old in long-term (20 d) test. The acclimatization time of the fish was two days before each test and the fish were fed daily with dry fodder.

The LC-50 tests were semi-static: half of the 50 liter water volume was changed daily. Fish density was 2 g l^{-1} water, dissolved oxygen concentration 70-90 % of ASV, water temperature 8-16^{o}C and pH 7.4.-8.4. The fish were not fed during the tests.

In the long-term test the water flow was continuous, with a theoretical exchange of 300 liter water volume every tenth hour. The fish density was 2 g l^{-1} water, dissolved oxygen concentration 60-90 % ASV and water temperature in the beginning of the test (October) 7.0-7.5^{o}C and at the end of the test (November) 1.5-3.0^{o}C. The effluent concentrations studied were 1 and 2.5 % (vol/vol).

The dilution water in the tests was the raw water used in the mill, taken from the Luodonjärvi freshwater reservoir. The quality of this water analysed before tests was as follows:

pH	6.3
conductivity	17.0 mS m^{-1}
alkalinity	0.05 mval l^{-1}
hardness	0.35 mmol l^{-1} Ca+Mg
$KMnO_4$-number	39 mg l^{-1}
sodium	15.0 mg l^{-1}
potassium	2.9 mg l^{-1}

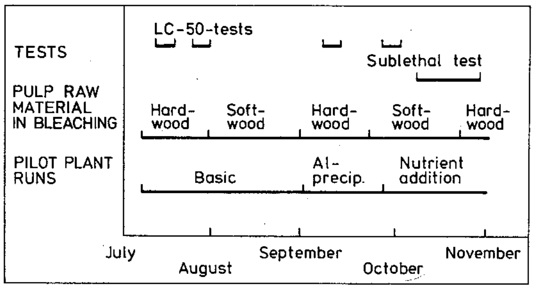

Fig. 6. Toxicity tests during different pilot plant runs.

iron	1.6 mg l^{-1}
aluminium	0.29 mg l^{-1}
copper	1.0 μg l^{-1}
zinc, cadmium and lead	< 1.0 μg l^{-1}
cobalt and nickel	<5.0 μg l^{-1}

The tests were carried out during debarking and bleaching operations and pilot-plant runs presented in Fig. 6.

Before the tests, combined effluent was filtered through a net (160 mesh). Effluents for the LC-50 tests were taken 24 hours before mixing owing to the high temperature of the water. Prior to mixing the effluent was aerated to 95 % of ASV with oxygen. Effluent to the storage tank of the long-term test was sampled three times a week.

The results of the LC-50 tests were calculated using the method of Finney (1972).

In the long-term test feeding of the fish was stopped three days before sampling. One day before sampling the fish were enclosed individually in restraining cylinders to avoid handling stress (Oikari and Soivio 1977). After stunning the fish by a blow to the head a blood sample was taken from the ductus Cuvieri into a heparinised syringe equipped with a hypodermic needle. The organs to be studied were dissected and preserved in liquid nitrogen. Bile samples were taken in the same way as blood samples and preserved as the dissected organs. After sampling the fish were deep-frozen for organoleptic studies.

The physiological parameters analysed for assessment of the response of fish to effluent were:

Condition (stress) parameters: Blood: haematocrite (Hct), leucocrite (Lct), haemoglobin (Hb), mean corpuscular haemoglobin concentration (MCHC). Plasma: glucose, lactate and protein contents, lactate dehydrogenase (LDH) activity (including H/M ratio indicating the possible targets of cellular injuries), K^+.

General metabolic parameters: Liver: somatic index (LSI), glycogen, lipid, protein and water contens. Blood: contents of glucose and lactate Plasma: Na^+, Cl^-, Ca^{2+}, Mg^{2+}.

Detoxification parameters: Liver and kidney: activities of UDP-glucuronyl transferase (UDP-GT) and β-glucuronidase (BG).

Neural function parameters: Brain: acetylcholine esterase (AChE) activity.

The analyses were carried out according to the procedures described by Oikari et al. (1979). The resin acid concentrations in fish blood plasma and bile extracts were analysed by the method presented by Oikari et al. (1980). The organoleptic analyses of fish were performed at the Technical Research Centre of Finland, Laboratory of Foodstuffs as presented by Kuusi (1973).

5.2 Results and discussion

A Probit-analysis was made of the primary results of the LC-50 tests. The LC-50 values were 19.7 % (vol/vol) for untreated and 98.1 % for treated effluent. The 95 % confidence limits were 8.7-44.7 % v/v and 93.2-103.3 % v/v respectively. Thus it can be estimated that the biological treatment decreased the short-term toxicity at least to one fourth of that of the untreated effluent. Walden and Howard (1974) obtained similar results. The short-term toxicity of neutralised untreated bleaching effluents was 15-50 %, whereas biologically treated effluent was acutely non-toxic.

The results of the analyses of plasma ions and tissue enzymes are presented in Fig. 7. No other parameter showed statistical difference. The physiological changes observed were similar to those observed in earlier experiments carried out in recipients receiving pulp and paper mill effluents (Soivio et al. 1979, Oikari et al. 1979). Response indicating possible tissue damage is increase found in plasma K^+ -ion content and activities of LDH and BG. Decrease found in the activity of UDP-GT indicates active function of detoxification prosesses inside fish. Increased activity of brain AChE enzyme may slightly deplete neural functions.

The plasma and bile extracts of control fish did not contain resin acids, while the total concentrations of resin acids in plasma and bile extracts of fish exposed to 1 % effluent were all below 60 mg kg^{-1} dry weight. The resin acid concentrations analysed in blood plasma and bile extracts of fish exposed to 2.5 % effluent, and the calculated reduction percentages in the treated effluent are presented in Table 8. All the concentrations in blood plasma extracts were below half of those in the bile extracts. The same tendency was observed in rainbow trout in recipient receiving kraft pulp mill effluents (Oikari et al. 1980).

According to chemical analyses the reduction of total resin acids in effluent during the long-term tests was 72 %, i.e. clearly higher than the 50 or 54 % calculated from the blood plasma and bile resin concentrations, respectively, of the fish. This indicates that the treated effluent also contained resin acids in amounts which were, even after further dilution, high enough to provoke the necessary active exrection of these toxic substances by the liver tissue. In this respect, the results agree well with the other physiological findings (Fig. 7).

The results of the organoleptic analyses are presented in Table 9.

The fish exposed to 2.5 % untreated effluent were judged unfit for human consumption. In addition, all the other fish except those of the control group and those exposed to 1 % treated effluent had to a greater or lesser extent an offlavour due to effluent.

Table 8. Concentrations (mg kg^{-1} dry weight) of different resin acids in the blood plasma and bile of fish and the calculated reduction percentages.

Sample	Pimaric	Isopimaric	Abietic	Dehydroabietic	Total
Untreated	2.5 %				
Plasma	19	44	29	166	260
Bile	88	105	75	401	670
Treated	2.5 %				
Plasma	30	30	32	42	130
Bile	38	35	57	181	310
Reduction	%				
Plasma	–	32	–	75	50
Bile	57	67	24	55	54
Water 1)	67	75	72	75	72

1) During the long-term test

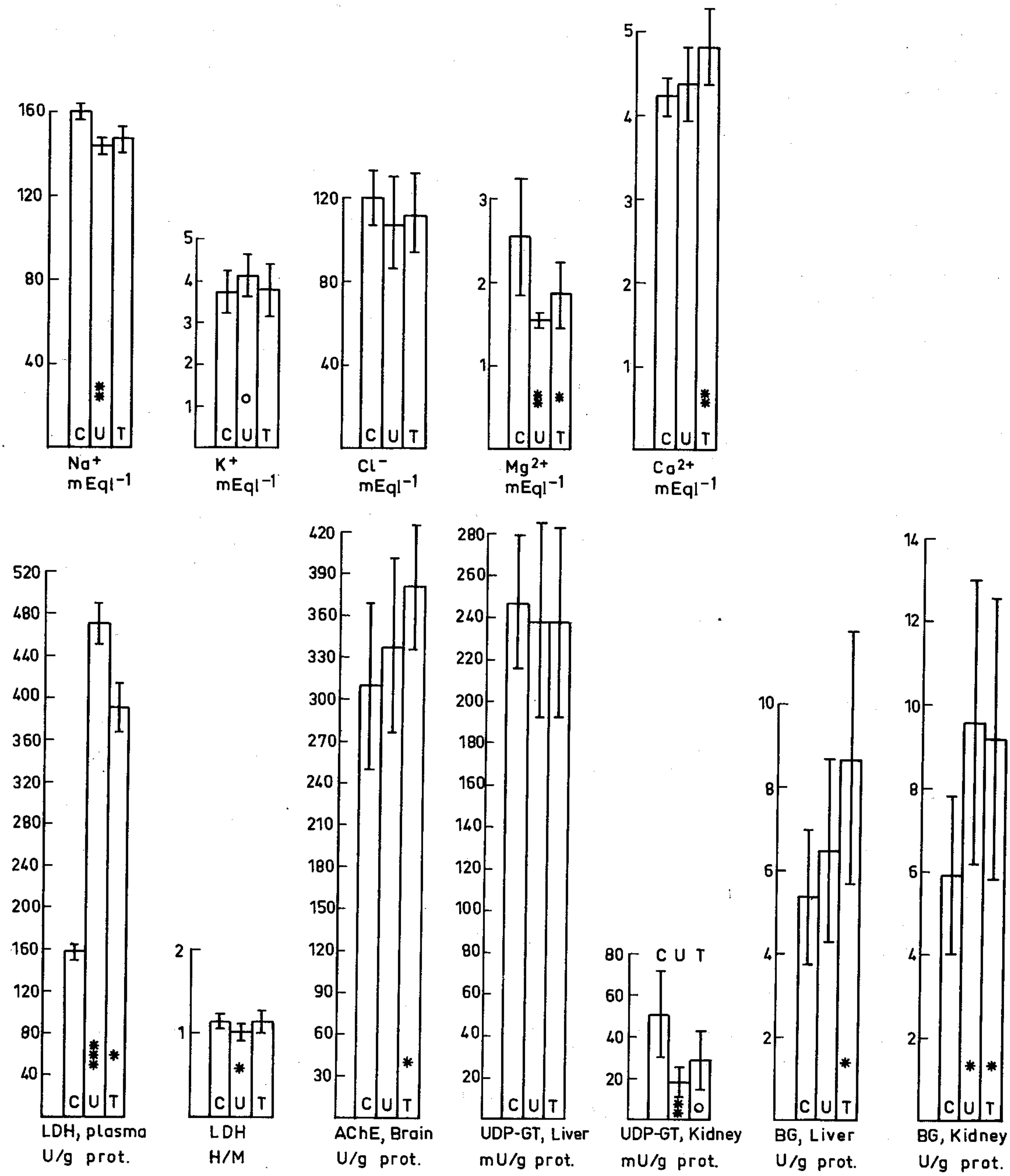

Fig. 7. Physiological responses of fish. Mean ± SD and statistical significance according to Student's t-test are indicated. C = control fish, U = fish exposed to 2.5 % untreated effluent and T = fish exposed to 2.5 % treated effluent. Statistical significance O = $P<0.1$, * = $P<0.05$, ** = $P<0.01$ and *** = $P<0.001$.

Table 9. Organoleptic scoring of fish fillets. The mean scores in the value ranges in parentheses are presented.

Sample	Raw		Cooked			Total scores
	Appearance (0–2)	Smell (0–4)	Appearance (0–2)	Smell (0–4)	Taste (0–10)	(0–22)
Control	1.7	3.5	1.9	3.7	8.0	18.8
1 % Untreated	1.5	3.3	1.7	3.3	6.6	16.4
1 % Treated	1.7	3.5	1.9	3.5	7.7	18.3
2.5 % Untreated	1.5	3.0	1.6	2.2	3.6	11.9
2.5 % Treated	1.7	3.3	1.9	2.9	6.2	16.0

6. SUMMARY

Pilot plant experiments using the activated sludge method were carried out to treat combined effluent from the bleaching and debarking processes of a kraft mill. In addition to conventional effluent parameters toxic compounds were also investigated. Toxic compounds were identified with gas chromatograph-mass spectrometer equipment. Fish tests were carried out in order to measure the overall toxicity of the effluent. The pilot plant was operated in three ways: first without addition of nutrients, secondly with optimum amounts of nutrients and thirdly with nutrient addition and simultaneous addition of precipitation chemicals.

The reduction in biological oxygen demand (BOD_7) was 70-80 % in undisturbed opearational circumstances. At the end of the experiments a strong and rapid fall in temperature caused considerably poorer purification results.

During the periods of nutrient addition the phosphorus content increased by about 1-2 mgl^{-1} in treated effluent. The purification process itself had only small effect to the phosphorus content.

Colour removal was not succesful with aluminium sulphate because the sludge became difficult to settle. This also led to poor results in the other parameters.

Resin acids, an important group of toxic compounds, were reduced without nutrient addition by 66 % on average, with nutrients by 72 % and with aluminium sulphate addition by 38 %. The reduction was best with addition of nutrients, and also showed least variation. The reductions of different resin acids showed no considerable differences. The proportion of dehydroabietic acid was the greatest, i.e. about half of the total resin acids.

Chlorinated phenolics, another important group of toxic compounds, were reduced by various degrees in the pilot plant. Without nutrient addition the reduction was 40 %, with nutrients 20 % and with aluminium sulphate addition 14 %. The reduction was very much dependent on the chlorinated compound itself and was in some cases as high as about 60 %. The amount of chlorinated phenolics in the influent was about one tenth of the amount of resin acids. The most important chlorophenols, ranked by concentration were, trichloroguaiacol, 2, 4, 6-trichlorophenol, trichlorodimethoxyphenol, trichlorocatechol and dichlorocatechol. The dichlorocatechol content of the effluent was often higher than that in the influent, which propably indicates that some chlorinated phenolics were converted to dichlorocatechol in the biological purification process.

The reduction of fatty acids and sterols was somewhat less complete than that of resin acids. During the overall period the reduction of fatty acids was 53 % and that of sterols 54 %. Betuligenol, ketobetuligenol, epoxystearic acid and quiacol were reduced well in the activated sludge pilot plant. Their reduction was 70-85 %.

During the period when aluminium sulphate was added the reduction of toxic compounds, as well as the BOD_7-reduction was poor because the sludge settled very poorly.

Good reduction of resin acids was also indicated by the analyses of these compounds in the bile and blood plasma of rainbow trout. In fish exposed to treated effluent the concentrations were only half of the concentrations measured in fish exposed to untreated effluent.

Acute toxicity of the waste water to fish was reduced considerably (about 50-70 %) by purification.

Biochemical and physiological analyses in a long-term test of three weeks revealed similar changes to those observed earlier in recipient tests. However, clear differences in long-term toxicity could not be found between treated

and untreated wastewater at the concentrations investigated (1.0 and 2.5 %).

The long-term test indicated that the purification of waste water considerably reduced smell and tase defects in the fish.

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LOPPUTIIVISTELMÄ

Pienoispuhdistamokokeita valkaisimo- ja kuorimojätevesien puhdistamiseksi aktiivilietemenetelmällä tehtiin noin puolen vuoden ajan sulfaattisellutehtaalla. Puhdistettavassa jätevedessä kuorimon selkeytetyn ja valkaisimon jätevesien suhde oli noin 5 : 4.

Kokeissa päästiin normaalikuormitteisella aktiivilietemenetelmällä häiriöttömissä oloissa noin 60-80 % biologisen hapenkulutuksen vähenemään (BOD_7).

Myrkyllisistä yhdisteistä hartsihapot, jotka olivat peräisin pääasiassa kuorimosta, vähenivät hyvin (75 %). Kloorifenolien vähenemä sen sijaan oli huomattavasti pienempi (30-40 %). Ajoittain kuitenkin myös kloorifenolien vähenemä oli suhteellisen hyvä (n. 60 %).

Jätevesien myrkyllisyyttä tutkittiin myös kalatestein. Puhdistus vähensi jätevesien akuuttia myrkyllisyyttä 50-70 %. Hartsihappojen tehokas vähenemä voitiin havaita myös kolme viikkoa altistettujen kalojen sisäelimistä tehdyistä analyyseistä. Puhdistetussa jätevedessä altistettujen kalojen sapessa ja veriplasmassa hartsihappopitoisuudet olivat noin 50 % puhdistamattomassa altistettujen kalojen vastaavista pitoisuuksista.

Kolme viikkoa altistettujen kalojen verestä ja kudoksista tehdyissä kliinisissä analyyseissä voitiin havaita samantapaisia muutoksia kuin aikaisemmin vesistöissä tehdyissä kokeissa. Puhdistamattomalla ja puhdistetulla jätevedellä ei kuitenkaan tässä suhteessa voitu havaita kovin selviä eroja.

Kaloille tehtiin lisäksi aistinvaraiset haju- ja makutestit. Testien perusteella puhdistus vähensi huomattavasti jäteveden kaloille aiheuttamia maku- ja hajuhaittoja.

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