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Studies of Transformation and Particle-Binding of Resin Acids During Oxidative Treatment of Effluent from Two New Zealand Pulp Mills

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Abstract Reactor studies of aerobic degradation of effluent from the first and last ponds of the treatment system of two New Zealand pulp and paper mills indicated that filterable BOD_5, resin acids and transformed resin acids, free and bound, degraded at similar rates. During oxidative treatment the resin acids of untreated effluent became increasingly bound to particulate material and a sediment high in abiet-13-enoic acid was formed.

Keywords Resin acid transformation · Particle-binding · Abiet-13-enoic acid · Pulp and paper effluent

In previous studies we have found that more than 90% of the resin acid content of primary clarifier effluent water generated by a kraft pulp and paper mill was either soluble or passed through a 0.05 μm membrane filter (Kanber et al. 2006). On the other hand, >70% of the extractable resin acids discharged from the biological treatment system and found in the Tarawera River, were bound to 0.05–15 micron particles (Ali-Kanber et al. 2000). While it can be anticipated that resin acids will bind with microbial biomass formed during oxidative treatment (Hall and Liver 1996), we wished to confirm this in controlled laboratory studies. In addition the role played by the particulate material remaining in the clarified primary effluent is not known. During treatment, conversion of abietic acid to abietan-13-enoic acid and abietan-18-oic acid occurs. A major component of the resin acid that survives aerobic treatment is particle bound abietan-18-oic acid (Kanber et al. 2006) consistent with earlier detection of saturated resin acids and resin hydrocarbons in the Tarawera River (Wilkins and Panadam 1987).

In the present studies we monitored the aerobic degradation of filtered and unfiltered effluent from the first pond of the four pond treatment system and unfiltered effluent from the final discharge to determine the relative degradation rates of the various resin acids present, the effect of particle binding on degradation and the relative degradation rates of resin acids and BOD_5 present in dissolved and particulate forms.

Materials and Methods

Water samples in screw capped 2.5 L glass winchesters or 20 L plastic containers were collected from the outflow of treatment ponds 1 and 4 of the combined treatment system for two pulp mills located on the banks of the Tarawera River, North Island, New Zealand (Ali-Kanber et al. 2006).

Bench reactor studies were performed in a 20 L vessel thermostated at 25°C containing 10 L of sample through which air was gently purged to maintain close to saturated aerobic conditions while providing gentle agitation. BOD_5 and resin acids were monitored over the 17–31 day duration of the experiments. The principal series of experiments involved sampling pond 1 and pond 4 (on different dates) and performing reactor runs with unfiltered (UF) or glass fibre filtered (GFF) samples. Reactor runs were typically initiated within 8 h of sampling. Prior to the withdrawal of analytical samples, the reactor vessels were removed from the water bath, thoroughly shaken and allowed to stand for 10 min at room temperature. The analytical sample (100 mL collected after discarding the first 20 mL) was withdrawn from a tap located 35 mm from the bottom of

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Table 1 Resin acid levels (µg/L) and BOD5 (mg/L) determined for UF Pond 1 water collected 27/1/2000, and subsequently aerated at 25°C for 31 days

	Seco	Pim	18-Ab	DHAA	13-ene	Ab	Cls	Total	BOD_5
L/L UF									
Day 0	606	1819	98	4591	1409	21	132	8676	96.3
Day 1	581	1765	16	4986	602	–	159	8109	86.3
Day 2	470	1523	51	4436	828	–	121	7428	78.5
Day 3	494	1544	16	4294	864	–	112	7323	71.4
Day 4	390	619	7.7	2324	648	–	89	4077	60.0
Day 7	345	95	5.1	220	121	–	17	803	30.0
Day 10	227	96	–	93	14	–	6.8	436	22.5
Day 16	23	55	–	41	77	–	4.6	200	19.0
Day 21	11	24	4.6	32	38	–	1.5	112	16.8
Day 31	15	16	34	19	9	–	2.0	96	
L/L 0.45 µm									
Day 0	471	1588	55	4662	876	–	119	7770	
Day 1	456	1479	12	4363	874	–	108	7292	
Day 2	404	1194	11	3900	542	–	73	6125	
Day 3	368	1105	12	3033	520	–	68	5105	
Day 4	383	1072	36	2187	466	–	73	4216	
Day 7	314	805	–	183	71	–	10	1383	
Day 10	136	28	–	39	18	–	2.0	223	
Day 16	5.9	8.9	–	18	10	–	0.8	44	
Day 21	6.2	7.3	–	19	8.1	–	–	41	
Day 31	15	5.5	–	16	–	–	1.0	37	
Sox 0.45 µm									
Day 0	77	320	2.2	450	246	–	43	1139	
Day 1	71	298	2.4	424	244	–	42	1081	
Day 2	54	234	2.1	345	166	–	33	835	
Day 3	53	244	2.6	345	173	–	33	851	
Day 4	31	139	0.9	157	86	–	18	432	
Day 7	33	105	0.9	44	29	–	3.5	215	
Day 10	31	78	–	56	27	–	4.0	196	
Day 16	19	29	–	17	26	–	0.4	92	
Day 21	11	21	–	12	18	–	1.5	64	
Day 31	7	15	–	11	13	–	0.5	47	

Abbreviations: L/L = liquid/liquid, UF = unfiltered, Sox = Soxhlet, Seco = secodehydroabietic acids-1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Ab = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids

the vessel. Samples were taken at regular intervals from the start of the reactor runs. For the UF experiment three sub-samples were withdrawn. One was extracted without filtration. The second was 0.45 µm filtered and the filtrate and filter paper liquid/liquid extracted, and Soxhlet extracted, respectively to determine resin acid levels using the GC/MS protocols reported previously (Ali Kanber et al. 2000). The third was used for BOD_5 measurement (APHA 1985). At the end of the trial, the remaining 400 mL of solution containing sediment precipitated during the trial was analysed in a similar manner. For the GFF experiment, sub-samples were taken after various incubation times and used for resin acid and BOD_5 determination without further filtration.

Pond 4 experiments were performed with only an UF effluent. At each sampling time, five 100 mL sub-samples were taken. The first was liquid/liquid extracted for resin acid determination. The second was used for BOD_5 measurement. The third was filtered through 0.45 µm filter paper, prior to liquid/liquid or Soxhlet extraction of the filtrates and filter papers respectively for resin acid determination. The fourth and fifth were combined and the 0.45 µm filtrate used for BOD_5 determination.

Results and Discussion

Resin acid and BOD data for the UF and GFF experiments for Pond 1 effluent are summarised in Tables 1 and 2. As is clear from Figs. 1 and 2, a generally similar decrease of BOD_5 and resin acids occurred. However in the UF system the rate of resin acid degradation appeared to increase after 4 days whereas in the GFF system the onset of increased degradation rate appeared to be delayed until day 7 and even longer for the minor secodehydroabietic acid components. Filtration may have removed active microbial biomass needed for degradation.

It is clear from the difference in the BOD_5 values of Tables 1 and 2 that glass fibre filtration before the commencement of the reactor experiments reduced the BOD_5. Furthermore, the BOD_5 difference decreased at a slower rate than the BOD_5 of the filtered system, indicating a slower rate of degradation of the particulate matter removed by filtration. Visible sediment was formed in the UF system from about day 5 while very little sediment formed in the GFF system. Data for the 400 mL slurry remaining at the end of the UF experiment are summarised in Table 3. The high levels of resin acid, the majority of which is abiet-13-enoic acid, are almost all associated with particulate material. Weight loss on ignition revealed that the particulate material was predominantly organic. SEM examination showed aggregates clumped around fibrous material.

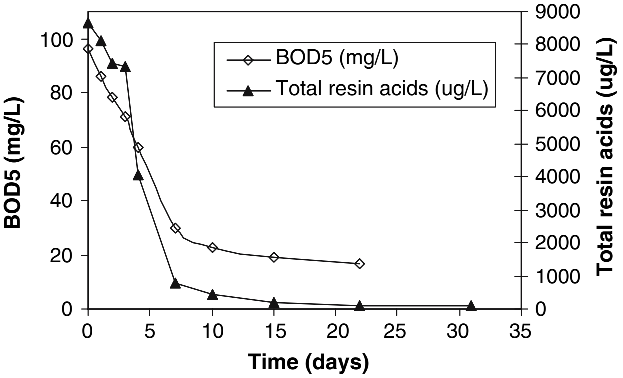

Fig. 1 BOD_5 and total resin acid levels determined for UF Pond 1 water collected 27/1/2000

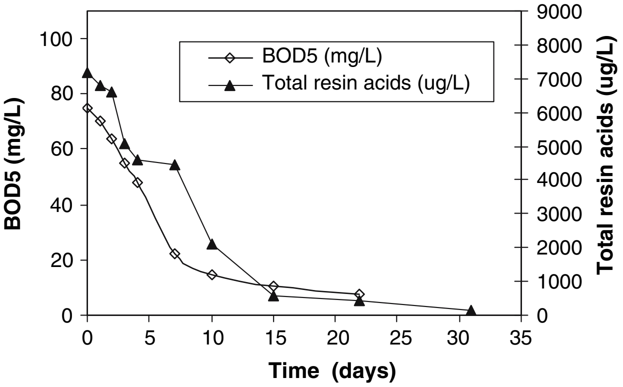

Fig. 2 BOD_5 and total resin acid levels determined for a GFF Pond 1 water sample, collected 27/1/2000

Figure 3 shows that the percentage of particle-bound resin acids in UF Pond 1 water increases as the total resin acid decreases during aerobic degradation. The effect became pronounced after day 4 when the majority of the resin acids had been degraded. In the case of the Pond 4 samples, much of the BOD_5 and resin acid was particulate

Table 2 Resin acid levels (µg/L) and BOD_5 (mg/L) determined for liquid/liquid extracted GFF Pond 1 water collected 27/1/2000 and subsequently aerated and incubated at 25°C for 31 days

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	Total	%	BOD_5
Day 0	441	1399	–	4379	854	93	7166	100	75
Day 1	389	1324	12	4369	613	91	6798	95	70.1
Day 2	402	1282	15	4289	516	86	6589	92	63.7
Day 3	368	1292	7.3	2791	531	77	5066	71	55.2
Day 4	326	898	10	3194	93	71	4592	64	48
Day 7	342	777	8.2	3178	45	91	4442	62	22.5
Day 10	449	(1314)[a]	4.3	192	67	63	2090	29	14.7
Day 16	416	58	4.7	47	20	30	575	8	10.6
Day 21	380	22	–	28	18		447	6	7.7
Day 31	51	18	–	39	18	2.8	129	2	

[a] Result may be anomalous. Abbreviations: GFF = glass fibre filtered, Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = % remaining relative to GFF water, measured on day 0

Table 3 Resin acid and levels (µg/L) and BOD_5 (mg/L) identified in the slurry remaining from the UF Pond 1 incubation experiment

Sample	Seco	Pim	18-Ab	DHAA	13-ene	Cls	Total	BOD_5
L/L UF slurry	234	833	5.9	634	1399	66	3173	38.5
L/L 0.45 µm filtrate	3.4	11	–	15	20	–	49.4	6.0
Sox 0.45 µm residue	280	819	11	560	1583	72	3325	

Abbreviations: L/L = liquid/liquid, UF = unfiltered, Sox = Soxhlet, Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids

at the time of sampling. Data for the distribution of BOD_5 and resin acids over various particulate size fractions are given in Tables 4 and 5.

The degradation of the bound and unbound components in the Pond 4 samples was monitored by reactor studies using unfiltered Pond 4 water, withdrawing duplicate samples and filtering one of these through 0.45 µm before analysis. The decrease of the bound and unbound resin acid and BOD_5 is summarised in Table 6. All the resin acids decomposed with similar kinetics. The degradation rates of free and bound components of the DHAA group, pimaric acid and abietan-18-oic acid were also very similar. Although abietan-18-oic acid is the principal survivor of the mills' treatment process, under the conditions of the experiment it degraded at the same rate as the other resin acids. Causes other than enhanced stability (under aerobic conditions) need to be found to explain the high levels of abietan-18-oic acid in the final discharge of the treatment system. It is of note that abietan-18-oic acid, abiet-13-enoic acid and dehydroabietic acid are the dominant resin acids in biologically treated effluents discharged by the mills to the Tarawera River. These resin acids are also the dominant constituents of biologically treated effluents discharged by another New Zealand pulp mill (Zender et al. 1994). On the other hand dehydroabietic acid and abietic acid, typically have been the dominant resin acids reported in treated or untreated effluents discharged by overseas pulp mills (McLeay 1987; Kostamo et al. 2004). The pathway that initially affords abiet-13-enoic acid and subsequently abietan-18-oic acid appears to be one primarily associated with the biological treatment regimes of New Zealand pulp mills, although intriguingly abietan-18-oic acid can be viewed as the immediate precursor of fichtelite (the decarboxylated analogue of abietan-18-oic acid). Fichtelite has been reported world-wide in historic sediments known to have natural inputs from woody plants (Otto and Simoneit 2001) and has been detected in Northern Hemisphere sediments affected by pulp and paper discharges (Leppanen et al. 2000).

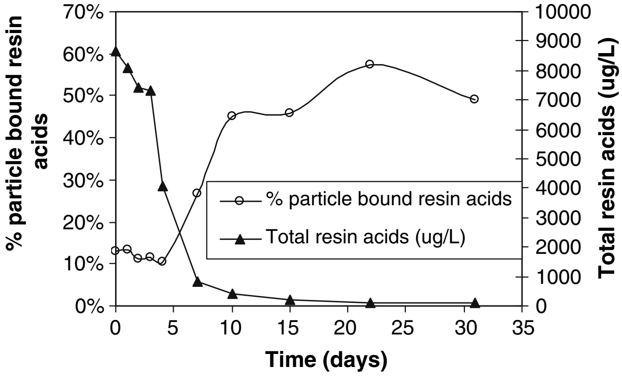

Fig. 3 Comparison of total resin acid degradation curves for UF Pond 1 water and percentage particle bound resin acids

Our results show that particulate matter provides a long lived BOD component in the Pond 1 water. Individual resin acids, including abietan-18-oic acid, and BOD_5 in 0.45 µm filtered samples, all undergo aerobic degradation with similar kinetics. Abietan-18-oic acid levels do not increase under these conditions but the percentage of particle bound resin acid, the majority of which is abiet-13-enoic acid, increases to about 50% of the total after 4–10 days. Related results for sediments recovered from treatment ponds and river sediments, including core samples (Wilkins et al. 1996; Judd et al. 1996) support the view that, at least for the biological regimes active in the New Zealand environment, the conversion of abiet-13-enoic acid to abietan-18-oic acid (Ali-Kanber et al. 2006) is promoted by the anaerobic conditions (Tavendale et al. 1997), such as those encountered in pond sediments. Apparently the conditions (aerobic) in our experiments were not conducive to the formation of abietan-18-oic acid. SEM evidence suggests

Table 4 Levels of BOD_5 (mg/L) in freshly collected and sequentially filtered Pond 4 water sample collected 1/11/99

	BOD_5	%
UF Pond 4	28.6	100
GFF Pond 4	15.5	54
3 µm	15.5	54
0.8 µm	14.3	50
0.45 µm	11.0	38

Abbreviations: UF = unfiltered, GFF = glass fibre filtered

Table 5 Levels of resin acids (μg/L) in freshly collected and sequentially filtered Pond 4 water sample, collected and extracted 1/11/99

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	Total	%
UF Pond 4 (a)	64	74	337	152	203	20	850	
UF Pond 4 (b)	68	77	364	158	211	20	898	
Average (n = 2)	66	75	350	155	207	20	874	100
GFF Pond 4 (L/L)	40	33	102	72	69	5	322	37
3 μm (L/L)	28	25	65	61	55	0	234	27
0.8 μm (L/L)	29	26	63	65	59	0	242	28
0.45 μm (L/L)	28	22	55	58	42	0	205	23

Abbreviations: UF = unfiltered, GFF = glass fibre filtered, L/L = liquid/liquid, Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water

Table 6 Levels of total, free and particle bound resin acid (μg/L) and BOD_5 in Pond 4 water sample collected 22/6/2000 and monitored over 17 days of aerobic treatment

Time (days)	Seco	Pim	18-Ab	DHAA	13-ene	Cls	Total	%	BOD_5
Unfiltered water									
day 0 (8 h)	241	297	480	354	983	5.8	2360	100	38.3
day 2	211	251	509	363	639	6.4	1980	84	32.6
day 3	132	155	307	314	557	5.2	1471	62	22.8
day 4	103	131	254	279	488	7.2	1262	53	15.1
day 7	23	64	98	127	199	0.5	511	22	9.1
day 13	12	41	59	79	134	0.7	326	14	8.1
day 17	14	45	58	66	87	0.3	271	11	nd
L/L 0.45 μm									
day 1	115	70	106	146	363	5.9	806	34	
day 3	87	61	97	158	138	5.7	545	23	
day 4	69	53	99	158	123	8.4	510	21	
day 7	14	16	20	59	37	1.1	147	6	
day 13	3.3	6.5	7.5	17	16	0.8	52	2	
day 17	1.3	3.7	4.7	7.2	9.4	0.8	27	1	
Sox 0.45 μm									
day 1	69	135	436	400	394	0.2	1435	61	
day 3	60	90	191	182	343	0.9	867	37	
day 4	32	65	141	147	195	0.2	580	25	
day 7	19	57	84	99	179	0.1	438	19	
day 13	9.2	36	47	54	116	0.0	262	11	
day 17	8.4	25	23	48	54	0.0	159	7	

Abbreviations: L/L = liquid/liquid, Sox = Soxhlet, Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = % remaining relative to UF water, measured on day 0, nd = not determined

that fibrous particulate material present in clarified effluent facilitates the aggregation and subsequent settling of biomass flocs. It is likely that the resulting pond sludges containing bound resin acid, particularly abiet-13-enoic acid, provide suitable anaerobic environments for the formation of abietan-18-oic acid.

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