

## Flocculation and filtration of effluent water samples

Sadiq A. Kanber<sup>1</sup>, Abudal Kadir A. Alnakshabandi<sup>2</sup>

<sup>1</sup> Medical Research Centre , Hawler Medical University

<sup>2</sup> College of pharmacy , Hawler Medical University

(Received: 11 / 5 / 2009 ---- Accepted: 5 / 1 / 2010)

### Abstract

The use of Polyferric sulfate (PFS) flocculation, followed by glass fibre filtration, reduced the levels of resin acids, colour and 5 Day biochemical oxygen demand (BOD<sub>5</sub>) in pond 1 water by more than 90% and appears to at least as effective as the existing secondary treatment system. This Observation indicate that primary flocculation/filtration technology could be as least as efficient as the existing secondary system process for resin acid, 5 Day biochemical oxygen demand (BOD<sub>5</sub>) and turbidity removal and more effective for colour removal. Preliminary cost estimates also indicate its probable cost effectiveness; this could be improved by the possibility of recovery or partial recovery and reuse of the flocculating agent.

**Keywords:** biological treatment system, flocculating agent and resin acids

### Introduction

In previous investigations more than 90% of the resin acid content of primary effluent water generated by pulp and paper mill processing operations are not associated with particles (1). On the other hand we have previously reported that > 70% of the extractable resin acids discharged from Tasman's biological treatment system, to the Tarawera River, were bound to 0.05-15 micron particles(2, 3).

It was therefore of interest to determine if the amount of particle associated resin acids, 5 Day biochemical oxygen demand (BOD<sub>5</sub>) and chromophoric species present in primary effluent water could be increased by treatment with flocculants. A combination of sedimentation and/or low cost filtration might then be used as a primary treatment, to replace or supplement biological treatment.

As effluent standards from pulp and paper mill wastewater treatment plants have become more stringent, the use of coagulants and/or flocculants as a tertiary treatment for bleached

kraft effluents has already been trailed. Scientists(4) have reported that polyacrylamide treatment of a bleached kraft effluent reduced the colour, chemical oxygen demand (COD), adsorbed organic halide (AOX), and 2,3,7,8-tetrachlorodibenzofuran and mixed-function oxygenase induction by 61%, 24%, 23%, 80% and 18% respectively.

The principle objective of the work reported in this paper was evaluation of the extent to which flocculating agents can remove resin acids, colour, 5 Day biochemical oxygen demand (BOD<sub>5</sub>) and turbidity from mill effluent prior to biological treatment

### Methods and Materials

Water samples in screw capped 2.5 L glass winchesters were collected from the outflow of the treatment pond 1 for two pulp mills located on the banks of the Tarawera River, North Island, New Zealand (1). Water samples were stabilized at the time of collection by the addition 0.1% of sodium azide (3) and stored at 4-8°C until required for analysis.

Pond 1 water samples (1 L) were flocculated using Polyferric sulfate (PFS) (10-60 mg/L), or Polyaluminum chloride PAC (10, 36 or 100 mg/L) at

pH 5.9-6.0. (PAC), or 5.1-5.3 (PFS). These pHs are similar to those found by several other authors (5,6); The flocculation process was monitored by particle size analysis. A portion of each of the thoroughly mixed flocculant solutions (1L) was sequentially filtered through glass fibre (1L), 0.8 µm (650 mL) and 0.2 µm (300 mL) filter papers. The pH of first portion (80 mL) portion of the filtrates was adjusted to 7, prior to resin acid, colour , turbidity analysis, which were performed (1, 7). The other portion was used for 5 Day biochemical oxygen demand (BOD<sub>5</sub>) measurement (8).

After removal of the 1L sample for sequential filtration, flocculated material was allowed to settle for 2-3 h. Precipitated material, recovered by sequential filtration, was transferred using a spatula to a 200 mL beaker and resolubilised in. 100 mL of distilled water by stirring at pH 10 and liquid/liquid extracted at pH 10 as reported previously (3).

### Results and discussion

The ability of flocculating agents or filtration, alone or in combination, to reduce resin acid and colour levels in untreated effluent water was investigated, it was envisaged that the application of these techniques might substantially reduce resin acid, colour, 5 Day biochemical oxygen demand (BOD<sub>5</sub>) and turbidity of the untreated effluent water. Effectively flocculation/ filtration would be used as a primary treatment step. This possibility does not appear to have been extensively investigated.

Pond 1 outlet water was used in these experiments since it was the first point in the treatment system from which a total effluent sample (comprised of clarifier and bleaching effluents) could be collected (1)

In order that some information might be obtained concerning changes in speciation effects during flocculation experiments, filtrates from the flocculation experiments were filtered sequentially through glass fibre (10 µm), 0.8 and 0.2 µm filter papers.

Resin acid results obtained using Polyferric sulfate (PFS), coagulation followed by glass fibre, 0.8 or 0.2 µm filtration are presented in Table 1. These results can be compared to those obtained in the absence of flocculant. Colour, turbidity and 5 Day biochemical oxygen demand (BOD<sub>5</sub>) levels were also determined for each of the filtered wastewater samples (Table 2).

**Table 1. Resin acid levels ( $\mu\text{g/L}$ ) determined for sequentially filtered natural and PFS (10-60 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.**

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
<b>No flocculant</b>								
pond 1 (A)	559	1647	19	4770	1700	160	8855	
pond 1 (B)	573	1803	14	4439	1984	164	8977	
mean ( $n = 2$ ) <sup>a</sup>	566	1725	53	4605	1842	162	8917	100%
glass fibre liq/liq	482	1264	12	4293	1125	99	7275	82% <sup>b</sup>
0.8 $\mu\text{m}$ liq/liq	488	1200	10	4634	938	86	7355	82%
0.2 $\mu\text{m}$ liq/liq	512	1172	10	4948	719	76	7438	83%
glass fibre Soxhlet	70	364	4.9	445	637	49	1569	18%
0.8 $\mu\text{m}$ Soxhlet	17	76	-	105	-	12	210	2.3%
0.2 $\mu\text{m}$ Soxhlet	18	69	12	83	91	7.5	280	3.1%
<b>10 mg/L PFS</b>								
glass fibre liq/liq	251	472	6.0	3190	698	32	4649	52%
0.8 $\mu\text{m}$ liq/liq	172	322	6.4	2306	155	23	2985	33%
0.2 $\mu\text{m}$ liq/liq	154	282	4.6	2102	172	18	2734	31%
glass fibre Soxhlet	194	710	6.3	1049	1058	84	3101	35%
0.8 $\mu\text{m}$ Soxhlet	7.2	21	0.7	40	2.5	2.9	74	0.8%
0.2 $\mu\text{m}$ Soxhlet	9.8	29	2.1	60	-	3.7	105	1.2%
<b>15 mg/L PFS</b>								
glass fibre liq/liq	243	544	12	2850	397	41	4087	46%
0.8 $\mu\text{m}$ liq/liq	194	391	4.8	2514	238	25	3367	38%
0.2 $\mu\text{m}$ liq/liq	167	306	3.5	2273	167	18	2935	33%
glass fibre Soxhlet.	208	852	9.8	992	1405	91	3558	40%
0.8 $\mu\text{m}$ Soxhlet	28	106	1.3	133	137	14	419	4.7%
0.2 $\mu\text{m}$ Soxhlet	5.7	26	-	47	-	2.7	81	0.9%
<b>20 mg/L PFS</b>								
glass fibre liq/liq	50.	76	4	1102	44	10	1285	14%
0.8 $\mu\text{m}$ liq/liq	45	68	6	961	34	9	1122	13%
0.2 $\mu\text{m}$ liq/liq	43.4	59	-	1007	-	8	1117	13%
glass fibre Soxhlet	445	1260	8	3087	1268	127	6196	69%
0.8 $\mu\text{m}$ Soxhlet	-	-	-	9	-	-	9.3	0.1%
0.2 $\mu\text{m}$ Soxhlet	-	-	-	19	-	-	19	0.2%

<sup>a</sup> mean of duplicate analyses, <sup>b</sup> recovery relative to unfiltered water Abbreviations: 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.

Polyferric sulfate (PFS) treatment (20 mg/L at pH 5.1-5.3) followed by glass fibre filtration removed 86% of the total resin acids, and 47%, 65% and 88% of colour at 270, 340 and 440 nm (Table 2) respectively.

It is apparent from the results presented in Tables 1 and 2 that soluble resin acids and colour present in pond 1 water is flocculated and becomes filterable by all of the doses used in these experiments.

However at the lower doses, the particles formed were smaller and smaller pore size filters were required for their removal. Above doses of 20 mg/L,

glass fibre (10 $\mu\text{m}$ ) filtration is adequate for efficient removal.

The results obtained using PAC, flocculation followed by glass fibre, 0.8 then 0.2  $\mu\text{m}$  filtration are presented in Table 3. The results can be compared with those obtained in the absence of flocculant. PAC treatment (100 mg/L, pH 5.9-6.1) followed by glass fibre filtration removed 56% of the total resin acids and 35%, 51% and 84% of colour at 270, 340 and 440 nm (Table 4) respectively.

**Table 2. Absorbance at 270 nm, 340 and 440 nm and turbidity (NTU) determined for PFS (10-60 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.**

	absorbance			% remaining <sup>a</sup>			Turbidity NTU	BOD <sub>5</sub>
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm		
no flocculant								
not filtered	2.242	0.884	0.319	100%	100%	100%	123	187
glass fibre	1.711	0.551	0.103	76%	62%	32%	13.3	93
0.8 µm	1.490	0.461	0.068	76%	52%	21%	5.24	77
0.2 µm	1.365	0.425	0.061	61%	48%	19%	2.37	62
10 mg/L PFS								
glass fibre	1.490	0.470	0.066	66%	53%	21%	10.2	65
0.8 µm	1.398	0.432	0.057	62%	49%	18%	2.17	49
0.2 µm	1.256	0.384	0.050	56%	43%	16%	1.57	47
15 mg/L PFS								
glass fibre	1.403	0.417	0.067	63%	47%	21%	7.73	45
0.8 µm	1.224	0.368	0.058	55%	42%	18%	0.90	42
0.2 µm	1.121	0.332	0.052	50%	38%	16%	0.46	39
20 mg/L PFS								
glass fibre	1.181	0.309	0.037	53%	35%	12%	1.32	22
0.8 µm	0.938	0.193	0.021	42%	22%	7%	0.75	18
0.2 µm	0.810	0.170	0.011	36%	19%	3%	0.61	12
25 mg/L PFS								
glass fibre	0.853	0.229	0.021	38%	26%	7%	1.34	17
0.8 µm	0.800	0.165	0.012	36%	19%	4%	0.58	14
0.2 µm	0.735	0.140	0.009	33%	16%	3%	0.45	13
30 mg/L PFS								
glass fibre	0.659	0.123	0.007	29%	14%	2%	0.64	15
0.8 µm	0.634	0.118	0.006	28%	13%	2%	0.36	13
0.2 µm	0.578	0.110	0.004	26%	12%	1%	0.21	10
40 mg/L PFS								
glass fibre	0.518	0.114	0.007	23%	13%	2%	0.54	5
0.8 µm	0.510	0.109	0.006	22%	12%	2%	0.33	3
0.2 µm	0.507	0.100	0.003	12%	11%	1%	0.43	-
60 mg/L PFS								
glass fibre	0.434	0.056	0.001	19%	6%	> 1%	0.54	5
0.8 µm	0.420	0.057	0.000	19%	6%	0%	0.32	3
0.2 µm	0.358	0.039	0.000	16%	4%	0%	0.47	-

<sup>a</sup> remaining relative to unfiltered water, normalise relative to unfiltered water.

**Table 3. Resin acid levels ( $\mu\text{g/L}$ ) determined for sequentially filtered natural and PAC (10-100 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.**

	Seco	Pim	18-Ab	DHAA	13-ene	ClS	total	%
No flocculant pond 1 mean (n = 2)	566	1725	53	4605	1842	162	8952	100%
10 mg/L PAC								
glass fibre liq/liq	403	939	7.8	3689	605	66	5709	64% <sup>a</sup>
0.8 $\mu\text{m}$ liq/liq	343	748	8.9	3343	478	47	4968	55%
0.2 $\mu\text{m}$ liq/liq	322	604	7.2	3221	318	35	4506	50%
glass fibre Soxhlet	119	544	3.3	534	853	66	2119	24%
0.8 $\mu\text{m}$ Soxhlet	20	83	-	79	65	10	258	2.9%
0.2 $\mu\text{m}$ Soxhlet	-	29	-	37	-	3.6	69	0.8%
36 mg/L PAC								
glass fibre liq/liq	353	778	5.9	3381	490	51	5059	57%
0.8 $\mu\text{m}$ liq/liq	352	211	7.8	3472	454	45	4541	51%
0.2 $\mu\text{m}$ liq/liq	272	173	5.4	2792	315	33	3590	40%
glass fibre Soxhlet	145	677	3.9	600	1019	79	2524	28%
0.8 $\mu\text{m}$ Soxhlet	-	17	-	21	17	1.5	57	0.6%
0.2 $\mu\text{m}$ Soxhlet	-	9.3	-	22	-	1.2	33	0.4%
100 mg/L PAC								
glass fibre liq/liq	260	513	4.5	2795	296	29	3899	44%
0.8 $\mu\text{m}$ liq/liq	234	428	6.5	2743	272	24	3708	41%
0.2 $\mu\text{m}$ liq/liq	206	358	5.7	2679	175	22	3446	38%
glass fibre Soxhlet	234	1029	6.0	1093	1436	104	3902	44%
0.8 $\mu\text{m}$ Soxhlet	2.8	8.5	2.3	15	7.5	0.8	37	0.4%
0.2 $\mu\text{m}$ Soxhlet	7.3	12	-	23	-	1.3	43	0.5%

<sup>a</sup> recovery relative to unfiltered water Abbreviations: 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 4. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for sequential filtration PAC (10-100 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.**

	absorbance			% remaining <sup>a</sup>			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	%
no flocculant not filtered	2.242	0.884	0.319	100%	100%	100%	123	100%
10 mg/L								
glass fibre	1.870	0.600	0.095	83% <sup>a</sup>	68%	30%	9.38	8% <sup>a</sup>
0.8 $\mu\text{m}$	1.848	0.588	0.094	82%	67%	29%	2.36	2%
0.2 $\mu\text{m}$	1.554	0.49	0.075	69%	55%	24%	0.56	2%
36 mg/L								
glass fibre	1.784	0.548	0.073	80%	62%	23%	3.06	2%
0.8 $\mu\text{m}$	1.544	0.479	0.069	69%	54%	22%	1.48	1%
0.2 $\mu\text{m}$	1.106	0.324	0.05	49%	27%	16%	0.96	1%
100 mg/L								
glass fibre	1.457	0.429	0.051	65%	49%	16%	3.41	3%
0.8 $\mu\text{m}$	1.354	0.399	0.050	60%	45%	16%	1.79	1%
0.2 $\mu\text{m}$	1.267	0.375	0.049	57%	42%	15%	0.67	1%

<sup>a</sup> remaining relative to unfiltered water.

The Soxhlet data (Table 3) obtained from the 0.8 and 0.2  $\mu\text{m}$  filter papers are anomalously low. Low data were also obtained if the filtrates were resolubilised at pH 10 and then liquid/liquid extracted. There is no apparent explanation for this anomaly.

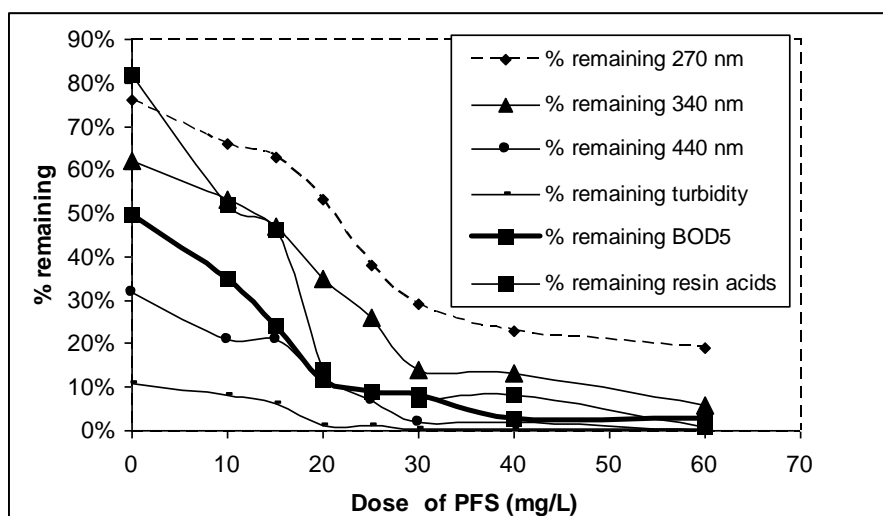
The extent to which PFS flocculation, in combination with glass fibre filtration reduced BOD<sub>5</sub> and turbidity was determined. Results are presented in Table 2.

A 20 mg/L dose of Polyferric sulfate (PFS), followed by glass fibre filtration, reduced colour at 440 nm and turbidity by 88% and 99% respectively, 5 Day

biochemical oxygen demand (BOD<sub>5</sub>) by 88% (Table 2).

The data presented in Table 1 can be compared with resin acid data presented in Table 2. It is clear that the

decline in 5 Day biochemical oxygen demand (BOD<sub>5</sub>) with increasing Polyferric sulfate (PFS) dose corresponds closely to that determined for resin acids (Figure 1).



**Figure1.** % Absorbances at 270 340 , 440 nm, resin acid, turbidity and BOD<sub>5</sub> determined for pond 1 water, collected 27/4/00, following treatment with various doses of PFS and filtration through glass fibre.

### Cost calculations

Using the data obtained from the flocculation/ filtration studies reported above it is possible to estimate the cost of Polyferric sulfate (PFS) required to treat Tasman's primary effluent. Assuming a daily discharge of 160 million L /day, a Polyferric sulfate (PFS) requirement of 20 mg/L comes to 3.2 tonne /day. At the bulk cost of Polyferric sulfate (PFS) (Orica Chemnet 2001) the chemical cost would be of the order of \$1.5 M/year. Any recovery of flocculant would reduce this chemical consumable cost.

### References

1. Kanber S. A., Langdon G Alan and Wilkins L Alistair, (2006). Particle Association of Resin Acids in the Biological Treatment of a New Zealand Pulp and Paper Mill. *Bull. Environ. Toxicol* 76, 3, 450-457.
2. Kanber S. A., Wilkins L Alistair and Langdon G Alan, (2000), Speciation of Pulp Mill Derived Resin Acids in the Tarawera River, New Zealand. *Bull. Environ. Toxicol*, 64, 622-629.
3. Kanber S. A., Langdon G Alan and Wilkins L Alistair, (2005) Speciation and stability of particle-bound pulp and paper mill sourced resin acids in sodium azide preserved recipient water. *Bull. Environ. Toxicol.*, 75, 135-142.
4. Hodgson, A. H., Hitzroth, A. J., Premdas, P. D., Hodson, P. H. and Duff, S. J., (1998). Effect of Tertiary Coagulation and Flocculation Treatment on

Other operating costs that would have to be met include the cost of granular media mining, preparation, transportation and disposal. Depending on the flocculation and filtration technologies chosen, other operating costs would be incurred. However, flocculation/ filtration treatment of primary effluent appears as an attractive option that warrants further investigation. It offers the possibility of reduced total effluent treatment costs (if it can take the place of secondary treatment) and improved effluent quality, particularly in regard to colour reduction.

- Effluent Quality from a Bleached Kraft Mill, *Tappi*, 81, 166-172
5. Beuulker, S. and Jekel, M., (1993). Perception and Coagulation of Organic Substance in Bleaching Effluent of Pulp Mills, *Water Sci. Technol.*, 27, 193-199.
6. Edzwald, J. K, (1993). Coagulation in Drinking Water: Particles, Organic and Coagulant, *Water Sci. Technol.*, 27, 21-35.
7. Kanber S. A., Langdon G Alan and Wilkins L Alistair, (2008). Studies of Transformation and Particle-Binding of Resin Acids during Oxidative Treatment of Effluent from Two New Zealand Pulp Mills *Bull. Environ. Toxicol*, 80, 2, 167-172.
8. APHA, (1985). *Standard Methods for the Examination of Water and Wastewater*, 16th ed., APHA, AWWA, WPCF, Washington, USA.

## تلبد وترشيح نماذج المياه المتدفقة

صادق علي قنبر ، عبد القادر عزيز نقشبندي

<sup>1</sup>مركز البحث العلمي ، جامعة هو لير الطبية

<sup>2</sup>كلية الصيدلة ، جامعة هو لير

( تاريخ الاستلام: 11 / 5 / 2009 ---- تاريخ القبول: 5 / 1 / 2010 )

### الملخص

ان استخدام تلبد متعدد كبريتات الحديد (PES) يعقبه ترشح باستخدام الزجاج المغزول قلل من مستوى الحوامض الرزينية، اللون ونقصان الاوكسجين البايوكيميائي لمدة خمسة ايام (BOD5) في حوض (1) بنسبه اكثر من (90%) وتظهر بكفاءة لاتقل عن كفاءة منظومه معالجه ثانويه موجوده. تبين هذه الملاحظات بان كفاءة تكنولوجيا التلبد الاولي/ الترشيح لاتكون اقل كفاءة من عمليه منظومه ثانويه لتقليل مستوى حامض الرزين ونقصان الاوكسجين البايوكيميائي لمدة خمسة ايام وازاله التعكر وكذلك هو اكثر كفاءة لازالة اللون. ان دراسه التكاليف الاوليه لهذه التقنيه تبين بانها ذات تكاليف جيده وهذه يمكن تحسينها باحتماليه اعاده تخليق او اعاده تخليق جزئي واعاده استعمال عامل التلبد.