COLOUR FORMATION IN PULP AND PAPER WASTEWATER TREATMENT SYSTEMS

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ABSTRACT

Pulp and paper wastewaters are coloured, and further colour can be formed during biological treatment. Colour discharge increases the attenuation of sunlight, thus affecting the ecology and aesthetics of the receiving water. The higher reported colour formation in activated sludge systems (AS) compared to aerated lagoons (AL) was studied. Colour behaviour in four laboratory-scale reactors, treating wastewater from a bleached kraft mill, together with a control treating a non-coloured synthetic wastewater, was monitored. Two reactors simulated well mixed AL operation at different hydraulic retention times (HRT), one the contribution of the sediment layer to ALs, and one an AS system. Results indicated that: (i) increasing aeration time increased colour formation, (ii) at short HRTs, increasing the sludge age did not increase colour formation, (iii) at longer HRTs, increasing the sludge age did increase colour formation, and (iv) activated sludge operation did not form colour, whereas colour approximately doubled in the aerated lagoon simulations, consistent with full-scale observations. One mechanism for colour formation in aerated lagoons may occur through the adsorption of colour precursors from the wastewater with subsequent intracellular microbial transformations. On settling, the formed colour may be released back into the wastewater where it may undergo further transformation.

KEYWORDS

Pulp and paper; aerated lagoon; activated sludge; colour formation; adsorption; biomass

1 INTRODUCTION

Wastewaters generated in the pulp and paper industry can be highly coloured, and wastewater colour is becoming an increasingly important regulatory concern both in New Zealand and internationally. Colour discharge into a receiving environment increases the attenuation of sunlight, thus affecting the ecology of the receiving water body, as well as having a major negative impact on its aesthetics. Reducing colour discharge requires a focus both on the colour discharged from the site, and on behaviour during biological treatment, as colour can be formed in secondary treatment systems. Where colour reduction at source is required to meet a certain discharge limit, it is important to understand what increase in colour may occur after the wastewater reaches the treatment system, allowing a colour reduction target to be accurately set. Where process changes are made to achieve colour reduction, it is also important to understand the impact of those changes on the colour compounds formed, as behaviour in the treatment system may change.

Pulping wastewaters contain lignin derivatives such as humic and fulvic acids, coloured compounds which give the wastewater its characteristic yellow-brown colour. These compounds are also implicated in colour formation in wetlands and natural water systems (Pinney *et al.*, 2000). There are many sources of colour around a pulp and paper mill, although the potential of individual streams to form colour is less well known. Colour loads vary with furnish (hardwood or softwood), mill type (chemical or mechanical, bleached, unbleached, or any combination thereof), bleaching sequence, degree of closure, and many other factors. The furnish dictates the type and quantity of coloured material produced. Hardwood processing produces a lower colour load than softwood processing (Wingate, 2002). The nature and behavior of the coloured material is also different. Wastewaters from bleached hardwood processing contain organics of a lower molecular weight and higher carboxyl group content than those found after softwood processing (Axegård *et al.*, 1993; Wallis and Wearne, 1994).

The most highly coloured waste streams within a chemical pulp mill are from the bleach plant. Within the bleach plant the alkaline extraction stream is often more highly coloured than the acidic stream (Table 1, Basta *et al.*, 1998). In this study, although the alkaline effluent had the highest colour load, it was the acid (chlorine dioxide stage) effluent which caused the greatest increase in colour during biological treatment. It has been estimated that 50% of the colour in bleaching wastewaters is due to quinones, 10% to other carbonyl related structures and 40% unidentified (Momohara *et al.*, 1989).

Table 1: BOD, COD and colour in bleach plant effluents from a chemical pulp mill (kg/ton)

Parameter (kg/ton)	Total bleach effluent	Alkaline effluent	Acid effluent	Acid effluent after 2° treatment
BOD_5	11	6	5	0.2
COD	62	38	24	12
Colour	51	36	17	22

Milestone *et al.* (2004) surveyed colour behaviour across twelve kraft pulp and paper mill treatment systems; nine were aerated lagoons (AL) and three were activated sludge (AS). Colour increased by 20 to 40% in the AL systems whereas the colour either remained stable or decreased in the activated sludge systems. Yousefian and Reeve (2000) found colour increases across biological treatment systems in only one of the four mills that they investigated. The other three mills they surveyed used activated sludge and did not have colour formation in their treatment system, regardless of wood type or chemical processing. In a laboratory simulation study, reported a colour increase in magnefite pulping effluents of up to 120% was observed depending on aeration (Casey *et al.,* 2003). Anaerobically treated wastewater from hemp pulping formed colour on treatment in a subsequent aerated pond (Kortekaas *et al.*, 1998).

There are several key differences between activated sludge (AS) and aerated lagoon (AL) operation (Table 2) which could be related to the observed differences in colour formation. Activated sludge systems operate at high biomass concentrations (up to 5 g/L), thus providing significant potential for colour adsorption. Aerated lagoon systems operate at low biomass concentrations (50 – 200 mg/L). Biomass is removed in a controlled fashion from an AS system and biomass generated in AL systems settles into an anaerobic sediment layer. Assuming some colour adsorbs onto the biomass in AL systems, then this colour will remain with the biomass in the sediment layer. It is possible that anaerobic breakdown of biomass could then release colour back into the overlying wastewater. Hydraulic retention times are very short (<1 d) in AS systems,

and considerably longer in AL systems (5 – 10+ days). If the colour formation mechanism were related to the aeration time, then higher levels of colour formation would be expected in AL systems. In AS systems, the solids retention time (SRT) is controlled separately from the HRT through sludge wastage, whereas in AL systems, the SRT is not controlled.

Although it has been reported that colour formation occurs across aerated lagoons and not in activated sludge plants, the mechanisms controlling colour behaviour are not well understood. Researchers have proposed different mechanisms, and it is likely that colour behaviour is controlled by a combination of competing mechanisms, which will vary in dominance depending on the treatment system environment (Liss and Allen, 1992; Pinney *et al*., 2000; Milestone *et al*., 2004, 2007). This study explored the following two scenarios with a particular emphasis on colour adsorption into the floc matrix: (i) colour formation in aerated lagoons is high as the wastewater is aerated for a relatively long time (5 - 10 days), and the sediment layer is also contributing colour released from the settled biomass, and (ii) colour formation in activated sludge is minimal as the wastewater is aerated for only a short time (up to 1 day), colour is adsorbed into the biomass matrix and removed through wasting.

Table 2: The key differences between activated sludge and aerated lagoon operation

Parameter	Activated sludge	Aerated lagoon
Hydraulic retention time (HRT)	Short (up to 1 day)	Long (5 – 10+ days)
Solids retention time (SRT)	5 – 10 days	Similar to HRT
Mixed Liquor Suspended Solids (MLSS)	1000 – 3000+ mg/L	25 – 100 mg/L
Solids accumulation	Minimal solids accumulation	Solids settle to base of lagoon
Mixing characteristics	Generally very good mixing	Often significant dead zones, and inefficient mixing

2 METHODOLOGY

2.1 WASTEWATER

The wastewater under study was the whole mill effluent from an integrated ECF bleached kraft mill pulping the softwood *Pinus radiata (BKME)*. Wastewater was collected as a single batch and stored at 4ºC until required.

2.2 REACTOR SETUP

Five 4L laboratory-scale reactors were operated in parallel, four on the BKME wastewater, the fifth on a synthetic wastewater, based on the composition of the mill wastewater, with no coloured material present. Two reactors were operated as Sequencing Batch Reactors (SBR) to simulate activated sludge operation. Two were operated as Continuously Stirred Tank Reactors (CSTR) to simulate well mixed aerated lagoon operation. One SBR was operated with only minimal solids removal to simulate the contribution of the sediment layer. The hydraulic retention times were set at 1 and 10 days, the solids retention times at 1, 10 and 100 days. Actual operating conditions differed from design (Table 3). The reactors treating the BKME were not seeded, rather the biomass present in the wastewater accumulated over time to form the mixed liquor suspended solids. The reactor operated on the synthetic wastewater was seeded with biomass from reactors already operating within the laboratory on a similar, non-coloured, wastewater composition.

Hence, this biomass had not been exposed to wastewater containing coloured compounds or colour precursors.

Table 3: Actual operating conditions for each reactor (± 95% Confidence Intervals)

Reactor	R1	R2	R7	R10
Volume (L)	4	4	4	4
Flow (L/d)	4.0 ± 0.6	4.1 ± 0.3	0.4 ± 0.1	0.4 ± 0.0
Waste (L/d)	NA	0.47 ± 0.02	NA	0.06 ± 0.04
HRT (d)	1.0 ± 0.2	1.0 ± 0.1	9.5 ± 0.6	10.3 ± 0.4
SRT (d)	1.3 ± 0.4	6.5 ± 1.1	9.7 ± 1.4	154.5 ± 163.7
DO (mg/L)*	2	2	2	2
Temperature (°C)*	30	30	30	30

*: Controlled to set point

Temperature (30°C) and oxygen levels (2 mg/L) were set to mirror full-scale operating conditions. Flow to each reactor was controlled using Masterflex peristaltic pumps and discharge was through a set overflow level. Each reactor was stirred at a rate sufficient to maintain the contents in suspension, and to minimise oxygen transfer at the surface. Dissolved oxygen was controlled via a variable speed air pump linked to feedback control through a dissolved oxygen probe. Temperature was maintained constant via heating coils within the reactor linked to feedback control through a temperature sensor. All wastewater feed and discharge was maintained at 4°C in a refrigerated cabinet beneath the reactor bank. The SBRs were operated with four cycles per day of 6 hours each. Waste volumes to achieve the desired solids retention times were removed from the reactor during the settle phase. The reactors were operated for seven weeks and then monitored closely for 2 weeks to establish steady-state performance.

2.3 WASTEWATER ANALYSIS

Wastewaters were analysed for the following parameters according to Standard Methods (APHA, 1998): Carbonaceous Biochemical Oxygen Demand ($cBOD_5$, 5210B); Total Kjeldahl Nitrogen (TKN), Dissolved Kjeldahl Nitrogen (DKN), Total Oxidised Nitrogen (NOx-N), Ammoniacal Nitrogen (NH_4^+-N), Total Phosphorus (TP) and Dissolved Reactive Phosphorus (DRP, 4500 series); Total Suspended Solids (TSS, 2540B). Dissolved Organic Carbon (DOC) was measured using an Elementar High TOC II analyser with autoinjector. The method used was an in-house method adapted from the manufacturers' instruction manual. The instrument complied with APHA requirements (Method 5310B, APHA 1998).

2.4 COLOUR MEASUREMENT

Colour was measured based on CPPA Standard Method (CPPA, 1993). Samples were filtered with 0.45 micron PES filters and pH adjusted to 7.6 with HCl or NaOH. Absorbance was measured at 465 nm and compared to a 500 mg/L chloroplatinate colour standard.

2.5 COLOUR EXTRACTION FROM BIOMASS

Mixed liquor containing biomass (100 mL) from each reactor including the control was filtered through GFC filter paper. The filter paper containing the biomass was steeped in 20 mL of 2 N NaOH for 24 hours, and the colour of the extract determined after pH adjustment to 7.6.

3 RESULTS AND DISCUSSION

Despite the broad range of operating conditions, all the reactors were able to remove the majority of the BOD, with 87 – 99% total BOD removal and 93 – 99% soluble BOD removal. Total organic carbon removals ranged from 55 – 71%, and dissolved organic carbon removals were slightly higher at 59 – 75% (Table 4). The reactors operating at the 10 day HRT achieved only slightly better performance than reactors operating at the 1 day HRT. The SBRs achieved higher mixed liquor suspended solids (MLSS) than the CSTRs as a result of cell recycle. Biomass yields were similar in the reactors operating at the shorter SRTs (R1, R2 and R7), but lower in the reactor operating at the extended SRT (R10) as a result of endogenous decay.

Table 4: Performance of the reactors treating BKME (± 95% Confidence Intervals)

	R1	**R2**	**R7**	**R10**
	CSTR	SBR	CSTR	SBR
HRT (d)	1.0 ± 0.2	1.0 ± 0.1	9.5 ± 0.6	10.3 ± 0.4
SRT (d)	1.3 ± 0.4	6.5 ± 1.1	9.7 ± 1.4	154.5 ± 163.7
MLTSS (mg/L)	73 ± 14	447 ± 104	87 ± 10	213 ± 24
TOC removal (%)	55 ± 4	62 ± 5	63 ± 6	71 ± 2
DOC removal (%)	59 ± 4	60 ± 4	75 ± 4	69 ± 1
BOD_T removal (%)	87 ± 30	92 ± 21	96 ± 8	99 ± 1
BOD_S removal (%)	93 ± 9	96 ± 3	99 ± 5	99 ± 1
Yield	0.50 ± 0.16	0.62 ± 0.10	0.68 ± 0.25	0.18 ± 0.20

3.1 COLOUR BEHAVIOUR

Colour behaviour in each reactor is given in Figures 1 and 2 on a concentration and mass basis respectively. The mass flows have been increased by a factor of 10 in Reactors 7 and 10 in order to compare the results directly. There was no significant difference in the colour entering the reactors over the course of the study ($p < 0.05$).

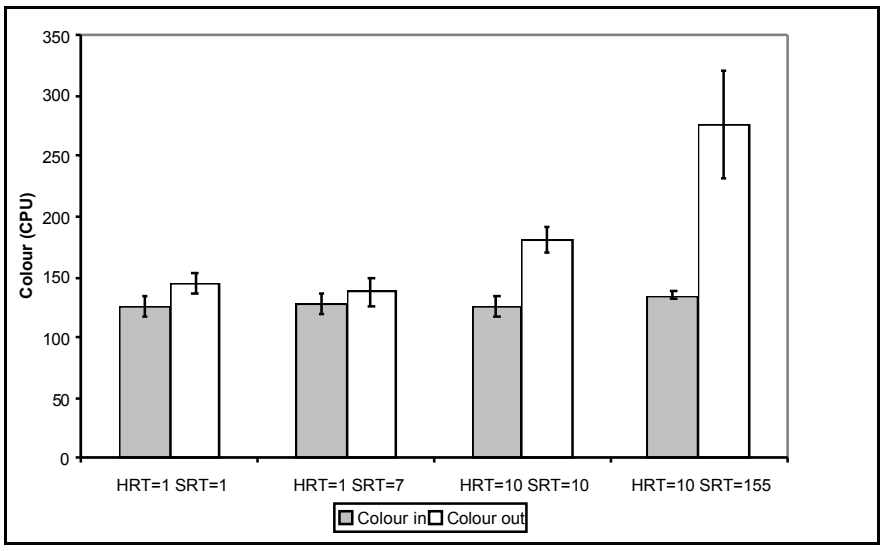

Figure 1: Colour entering and leaving each reactor on a concentration basis (mg/L). Error bars are 95% Confidence Intervals.

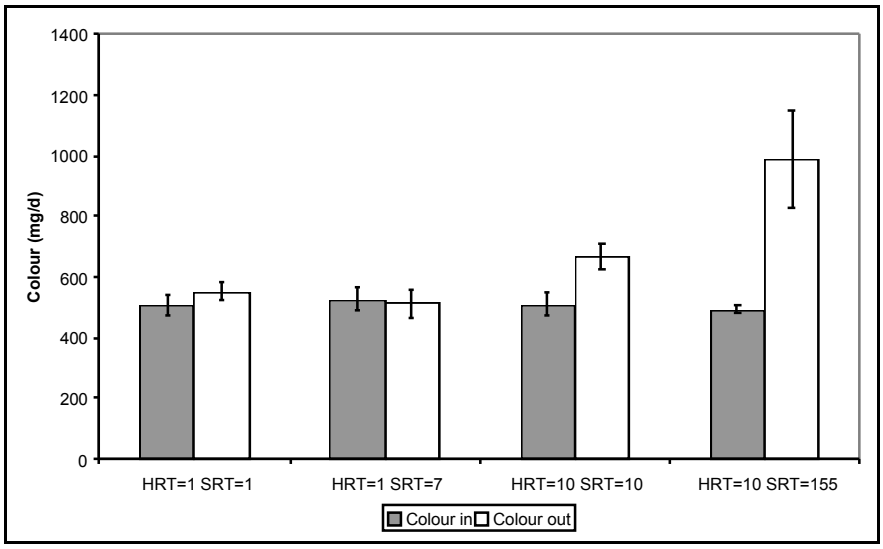

Figure 2: Colour entering and leaving the reactor on a mass basis. NB: Reactor 7 and Reactor 10 have been normalised to the flow entering Reactors 1 and 2. Error bars are 95% Confidence Intervals.

The colour leaving the reactors varied. At the 1 day HRT (SRT 1 day and 7 days), there was no significant difference in the colour entering and leaving the reactors, either on a concentration or mass basis ($p < 0.05$). Increasing the solids retention time did not increase the colour in the effluent. At the 10 day HRT, increasing the SRT did increase colour formation in the effluent. This increase in colour is likely to be due to a combination of the following factors: (i) endogenous decay of biomass releasing colour adsorbed onto the biomass matrix, and (ii) further oxidation of the colour released from the biomass matrix as a result of the longer HRT. Further research will be required to determine the exact mechanisms involved.

3.2 COLOUR ON BIOMASS

Visually, it was apparent that colour adsorbed onto the biomass in the reactors treating kraft effluent. Biomass in the reactor treating synthetic effluent under the same conditions was virtually colourless. Colour was extracted from the biomass in each reactor using NaOH, as well as the control reactor treating synthetic effluent (Table 5). Biomass from the 1d CSTR contained the most colour. Biomass from the two CSTRs contained more colour than the SBRs, with the 1 d SBR containing the least colour. Only a small amount of colour was extracted from the biomass treating the synthetic effluent (0.2 mg CPU/mg biomass).

Table 5: Colour extracted from the biomass in each reactor

Reactor	Effluent	Colour extracted (mg CPU/mg biomass)	Colour extracted corrected for control (mg CPU/mg biomass)
R1, HRT = 1 d, SRT = 1d	BKME	2.2	2.0
R2, HRT = 1 d, SRT = 7 d	BKME	0.5	0.3
R7, HRT = 10 d, SRT = 10 d	BKME	1.6	1.4
R8, HRT = 1 d, SRT = 10 d	Synthetic	0.2	
R10, HRT = 10 d, SRT = 155 d	BKME	1.0	0.8

3.3 COLOUR MASS BALANCE

A mass balance incorporating colour in the effluent and on the biomass was attempted (Table 6). The colour balances across Reactors 1, 2 and 10 were very similar at 106%, 108% and 118% respectively, indicating that overall the colour approximately doubled. Only the SBR, operated at a 1d HRT and 6.5 d SRT showed little colour change at 12%.

Table 6: Mass balance across the four reactors treating BKME

Reactor	Colour in (mg/d)	Colour out (mg/d)	Colour on biomass (mg/d)	Colour increase (mg/d)	Colour increase (%)
R1, HRT = 1 d, SRT = 1d	505	552	458	537	106
R2, HRT = 1 d, SRT = 7 d	527	511	80	64	12
R7, HRT = 10 d, SRT = 10 d	54	67	51	58	108
R10, HRT = 10 d, SRT = 155 d	49	99	6	58	118

In order to better understand the distribution of the colour, the proportion of colour change occurring in the effluent and on the biomass was explored (Table 7). In CSTR operation, there was a large increase in colour associated with the biomass. In SBR operation, the colour change associated with the biomass was much less.

Table 7: Percentage colour change in the effluent and on the biomass

		Colour change as a percentage of colour entering the reactor		
Reactor setup	Type	Effluent	Biomass	Total
R1, HRT = 1 d, SRT = 1d	CSTR	9%	97%	106%
R2, HRT = 1 d, SRT = 7 d	SBR	-3%	15%	12%
R7, HRT = 10 d, SRT = 10 d	CSTR	24%	84%	108%
R10, HRT = 10 d, SRT = 155 d	SBR	102%	16%	118%

The large proportion of the colour associated with the biomass at the 1d HRT/SRT suggests that the mechanism of colour formation was very rapid in the CSTR system. As there was no change in the wastewater colour between the influent and the effluent, this observation also suggests that non-coloured precursors from the wastewater were absorbed and metabolised, and colour formed within the biomass matrix. If CSTR operation at the 1d and 10d HRT is compared, it appears that some of the colour formed in the biomass was transferred back into the wastewater at the longer HRT. As the HRT/SRT was increased from 1d to 10d, there was a larger increase in colour associated with the effluent, and a smaller increase associated with the biomass, consistent with the hypothesis that colour is released on cell lysis at the longer SRT.

The highest effluent-related colour was observed in the 10d HRT/155d SRT SBR. The majority of the colour increase was associated with the liquid phase. The biomass yield in this system was much lower than the other systems, reflecting the high level of cell breakdown occurring at such a long SRT. This observation was also consistent with the hypothesis that colour precursors were adsorbed, with subsequent colour formation within the cell, and release back into the wastewater. The mass balance suggests that a small amount of further colour formation in the wastewater may have occurred. If it assumed that non-coloured precursors were adsorbed into the biomass matrix prior to colour formation, then this mechanism did not appear to occur in the 1d HRT/7d SRT

SBR. There was only a small amount of colour associated with the biomass in this reactor, and a slight decrease in the wastewater. There is no obvious explanation for the lack of colour formation in the biomass under these conditions.

In this study, activated sludge operation was simulated in the 1d HRT/7d SRT reactor, whilst aerated lagoon operation was simulated in the 10d HRT/155 d SRT reactor. This latter reactor retained the biomass in the system for very long periods of time, at least in part simulating the effect of cell breakdown at the sediment-wastewater interface. The differing colour behaviour between these two configurations was consistent with full-scale observations (Milestone, 2004).

It is hypothesised that one mechanism for colour formation in aerated lagoons may occur through the adsorption of colour precursors from the wastewater with subsequent microbial transformations within the cell. On settling, the biomass breaks down in the sediment layer, potentially releasing the formed colour back into the wastewater where it may undergo further oxidation and colour formation. More targeted studies, including the use of isotopically labelled quinones, are required to test the above hypothesis. Such an approach could demonstrate a positive link between wastewater precursors and formed colour.

4 CONCLUSIONS

This study tested the hypothesis that the differences in colour behaviour between activated sludge and aerated lagoons observed at full-scale are related to (i) the length of time the wastewater remains in the system (HRT) and (ii) cell lysis at longer SRTs causing the release of colour adsorbed from the wastewater into the biomass matrix. Results indicated that:

- The longer the aeration time, the greater the colour formation.
- At short HRTs, increasing the SRT did not increase colour formation in the effluent.
- At longer HRTs, increasing the SRT did result in colour formation in the effluent.
- There was more colour associated with the biomass under CSTR operation than under SBR operation.
- On a mass basis, the 1d HRT/7d SRT reactor did not appear to form colour, whereas all other simulations approximately doubled the influent colour.
- The colour associated with the biomass in a reactor receiving non-coloured synthetic wastewater was minimal.
- The aerated lagoon simulation exhibited colour formation, whereas the activated sludge simulation did not, consistent with full-scale observations.

More targeted studies, including the use of isotopically labelled quinones, are required to explore these findings in more detail.

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