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Colour formation from pre and post-coagulation treatment of *Pinus radiata* sulfite pulp mill wastewater using nutrient limited aerated stabilisation basins

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ABSTRACT

Potential short and long term effects of coagulated *Pinus radiata* (sulfite process) pulp wastewater mixed with uncoagulated paper mill wastewater on colour formation in aeration stabilisation basins were investigated by simulation studies. Changes in the character of organics in the simulated ASB treatments were assessed from changes in the molecular weight (MW) distributions of compounds that contributed to colour formation. Data from these simulations were also compared with data from the full scale ASB that was used to treat non-coagulated wastewater at the time of this study. The laboratory scale ASB treatment comprised two parallel sets of 3 tanks (Simulations A and B) that were operated over three hydraulic retention times (HRTs) of 84 days in total. The influent used for both simulations was post-coagulated pulp mill wastewater mixed with paper mill wastewater (1:2). Sludge collected from the full scale ASB pond system was correspondingly added to the tanks of both simulations for inoculation with indigenous microorganisms. In addition, settled sludge collected after coagulation of pulp mill wastewaters was added to Simulation B to investigate the effects of alum flocculated material. The wastewaters of Simulations A and B had $SUVA_{256\ and\ 280}$ values of between 1 and 2 while those of the full-scale system were between 2 and 4. Significant differences were found in colour formation between the two simulations. Peak fitting of HPSEC–UV chromatographs (260 nm and 280 nm) indicated removal of low molecular weight (LMW, <800 Da) UV absorbing compounds in ASB treatment. Colour was attributed to MW compounds of >800 Da. Peaks of HMW compounds, ~1718 and 1775 measured at 260 nm and 280 nm, respectively were significantly higher in Simulation A at the 1 and 3 HRT compared with Simulation B, which corresponded in higher colour formation in Simulation A. A survey of the full-scale ASB showed a significant decrease in MW of organic compounds throughout the treatment process, with colour formation apparent when compounds had a MW >3000 Da. These compounds were likely to be aromatic and lignin-derived. The addition of alum sludge had significant effects on the extent of colour development.

1. Introduction

Wastewaters from pulp and paper industries are characterised by high colour (brown to black), which is attributed to complex dissolved organic matter (DOM) [1,2]. The DOM present in these wastewaters exhibits a higher content of lignin derived aromatic organic compounds when compared with DOM from non-polluted waters [2].

Colour commonly increases throughout aerated stabilization basin (ASB) treatment systems, which may be due to the organic material being converted into smaller chromophoric units rather than being mineralised [3]. These coloured compounds may also

Abbreviations: Al^{3+}, aluminium; ASB, aerated stabilization basin; AMW, apparent molecular weight; BOD, biological oxygen demand (mg/L); DOM, dissolved organic matter; ^{13}C CP NMR, ^{13}Carbon cross polarization nuclear magnetic resonance; Da, Dalton; DOC, dissolved organic carbon; FS, full scale; FTIR, fourier transform infrared; FH, fluorescence humic-like material; HMW, high molecular weight; HPSEC, high performance size exclusion chromatography; HPLC, high-performance liquid chromatography; HRT, hydraulic retention time; HU, hazen unit; HS, humic substance; IR, infrared; LMW, low molecular weight; LS, laboratory scale; MW, molecular weight; SUVA, specific ultraviolet absorbance; TOC, total organic carbon; UV, ultraviolet.

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originate from those that are not removed during biological treatment [3,4].

Coagulation treatment is more efficient in removal of high molecular weight (HMW) DOM, than the low molecular weight (LMW) compounds [5,6]. Therefore, it might be expected that coagulation prior to ASB treatment would minimise colour development. In our previous work [7] it was determined that colour increases occurred in post-coagulated wastewater treated in a simulated ASB over 84 days (3× HRT) of continuous operation. This was attributed to compounds that were unable to be removed by coagulation, such as lignocarbohydrate derivatives and hemicellulose from the influent stream and organics produced by microbiota during treatment. Nonetheless, treatment by ASB under simulation conditions was found to remove ~95% of biological oxygen demand (BOD) [8] even under nutrient limited conditions [9].

The effect of direct coagulant addition to a secondary biological treatment stage, known as simultaneous precipitation, is well documented [10,11]. However, the effect of residual coagulant that remains in the supernatant prior the secondary biological treatment that undergoes simultaneous pre-precipitation has received little attention [5]. Lees et al. [5] found a relationship between low-level concentrations of coagulant and reduction in microbial activity. Yet, correlation between the simultaneous pre-precipitation of organics with colour development throughout the biological treatment process, has yet to be adequately investigated. For this to be done the application of analytical techniques for the quantification and characterization of organics during ASB treatment is warranted.

Elucidation of the character of organic compounds using resin fractionation, UV–Vis spectroscopy, high-performance liquid chromatography (HPLC), and high-performance size-exclusion chromatographic (HPSEC) with UV detection have been widely reported [12,13]. These methods have several advantages such as high precision absorbance measured with small sample volumes, molecular size or weight determinations can be made on whole water samples without pre-concentration and at the low cost compared with the other characterisation methods such as ^{13}C NMR, IR, FTIR [14,15].

UV–Vis spectroscopic techniques used to characterise organic compounds provide absorption spectra that are generally featureless, with absorbance typically decreasing with increasing wavelength [16,17]. For example, UV absorbance at 254 nm (UV_{254nm}) has been widely used to provide an estimate of the aromaticity of carbon compounds present in non-polluted waters [18], while UV_{280nm} has been used to study pulp and paper effluents for lignin derived [2] or humic substance (HS) contents [14]. Characterisation of organic compounds based on only a single wavelength reduces the amount of useful information that can be obtained from the entire absorbance spectra [15] and hence using multi-wavelengths enhances the information gained.

A key aim of the study reported here was to investigate changes in the character of organics in mixed pulp (sulfite) and paper mill wastewaters where coagulation was performed on the pulping wastewaters using alum. Changes in the character of organics were investigated in association with colour development in nutrient limited ASB treatment. This investigation utilised UV–Vis spectroscopy (multi-wavelength absorbance detection at λ 254, 280 and 456 nm), HPSEC–UV (260 and 280 nm) and HPSEC-Fluorescence with peak fitting (to resolve over lapping peaks of HPSEC spectra) for characterization of organic compounds.

The characterisation of organics present in post coagulated wastewaters of pulp *(Pinus radiata)* and paper mills during ASB treatment by HPSEC–UV absorbance and through assignment of resolved molecular weight (MW) peaks (by peak fitting) has not been widely investigated. The peak fitting technique was expected to be particularly useful for evaluating the changes in the MW of compounds that are aromatic structures that absorb UV light (UV_{254nm}) and lignin-like material (UV_{280nm}), which might contribute to the colour formation throughout the ASB treatment. Characterisation was performed on organics from the full-scale ASB (FS-ASB) under typical operation conditions to compare the potential effects of pre-coagulation on subsequent ASB treatment, in short and long term application.

2. Experimental

2.1. Survey of the full-scale mill ASB

Wastewater and sludge samples were collected from a FS-ASB of an integrated *P. radiata* pulp (sulfite) and paper mill located in southeast of South Australia (37°35′S 140°21′E). The pulp and paper mill produced ~30 mL per day of wastewater. At the time of this study, combined mill wastewaters were treated by a clarifier (7 h) followed by ASB treatment (comprising 3 ponds in series with the first two aerated) with 26–30 days hydraulic retention time (HRT). To characterise the organic compounds in the wastewater throughout the FS-ASB, a survey of the ponds was conducted at the same time as laboratory ASB simulation trials. The influent (after treated by the clarifier) and effluent samples from each pond were collected using a Van Dorn sampler, held in PET bottles (rinsed thoroughly with source water of the samples collected). Samples were then transported to the laboratory (cooled) and stored at ~4 °C until analysed.

2.2. Laboratory-scale ASB simulation trials

2.2.1. ASB simulation tanks

ASB simulations were conducted using tank dimensions that simulated a full-scale ASB (FS-ASB) system as previously described by Lewis et al. [7]. Each simulation system consisted of 3 ponds in series, i.e. Pond 1 (8.5 L, aerated), Pond 2 (5.6 L, aerated) and Pond 3 (8.6 L, un-aerated). A flow rate of 0.79 L/day provided the same HRT as the FS-ASB (28 days = 1 HRT) and these were continuously monitored for 3× HRT (1 HRT = 28 days; 2 HRT = 56 days; and 3 HRT = 84 days, respectively) at room temperature ~21 °C. Two series of simulation tanks were incorporated in this study.

Prior to investigations reported, the performance of the laboratory ASB system was tested under conditions that simulated the FS-ASB operations. The colour concentration of effluent from the laboratory scale ASB after 1 HRT was ~360 HU (at 456 nm), while the colour of effluent from FS-ASB averaged ~290 (range ~180–380 HU) over the previous 12 month period. Under laboratory test conditions, BOD removals were >95%, as of the FS-ASB treatments. Thus, colour formation and BOD5 removal were determined to be approximately similar between the laboratory scale ASB and the FS-ASB.

2.2.2. Influent wastewater

Two batches of coagulated (80 ppm of $Al_2(SO_4)_3{\cdot}18H_2O$ as Al^{3+} or 1860 ppm of alum) wastewater and alum floc sludge were sourced from a pilot scale coagulation plant operated on site at the *P. radiata* pulp mill (sulfite). At the same time, 2 batches of uncoagulated paper mill wastewater were also collected and stored at 4 °C before used. The coagulated wastewater was mixed daily with paper mill wastewater at a ratio of 1:2 immediately after reaching ambient temperature (15–21 °C) following storage at 4 °C. The mixed wastewater was then pumped continuously as influent to the laboratory scale ASBs, using a multiple-head Masterflex peristaltic pump (Model 7518-00). This ratio was based on the mix of wastewaters flowing into the FS-ASB at the time of this study. As part of assessment of influent wastewater quality,