Chemical Engineering Journal 175 (2011) 160–168

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Changes in the organic character of post-coagulated *Pinus radiata* sulfite pulp mill wastewater under aerated stabilization basin treatment—A laboratory scale study

Rosmala Lewis[a,*], John A. van Leeuwen[a], Ronald J. Smernik[c], Christopher W.K. Chow[a,b], Andrew Everson[a], S.C. Nothrop[a], Simon Beecham[a]

[a] *Centre for Water Management and Reuse, School of Natural and Built Environments, University of South Australia, South Australia, 5095, Australia*
[b] *Australia Water Quality Centre, South Australia, 5000, Australia*
[c] *School of Agriculture, Food and Wine, The University of Adelaide, Waite Campus, Urrbrae, South Australia, 5064, Australia*

ARTICLE INFO

Article history:
Received 23 March 2011
Received in revised form
16 September 2011
Accepted 20 September 2011

Keywords:
ASB
Coagulation
Pulp mill
Nutrient
Organic compounds

ABSTRACT

Treatment of wastewater from a *Pinus radiata* sulfite pulp and paper mill with coagulation followed by aerated stabilization basins (ASBs) was investigated to determine a treatment process that minimizes the colour formation. Two post-coagulation wastewaters were investigated, one low in P (Simulation A; BOD:N:P = 100:1.3:0.06) and the other higher in P but still moderately P-limited (Simulation B, BOD:N:P = 100:1.3:0.3). Changes in the organics character of the wastewaters were investigated at several stages of treatment: untreated, after coagulation; during and after ASB treatment, using HPSEC and solid-state ^{13}C CP NMR spectroscopy.

Effective reductions in colour$_{456\text{nm}}$, and UV$_{254\text{ and }280\text{nm}}$, (~80%) were achieved by coagulation using alum (1860 ppm). However, during ASB treatment, colour$_{456\text{nm}}$ increased (>100%) in both simulations. HPSEC analysis showed that removal of HMW (>3000 Da) was achieved through coagulation with the simultaneous removal of LMW (<300 Da) in the ASB simulations. Subsequent to the removal of HMW and LMW, an increase of intermediate-range compounds (300–3000 Da) occurred. Solid-state ^{13}C NMR analysis indicated some selective removal of aromatic and alkyl groups during the coagulation process and additional removal of aromatic C during ASB treatment.

The slightly higher proportion of HMW (>1000 Da) in ‘A’ than ‘B’ and the slightly higher proportion of aromatic C and alkyl groups remaining in the effluent of ‘A’ might be the basis for differences in the colour development in the two ASB simulators. The low nutrient loading (external) in the pre-treated wastewaters has been shown to be sufficient to sustain microbiological growth of organisms that contribute to colour formation with ASB treatment. This occurred in both simulations and it was concluded that the manipulation of the BOD:N:P ratio to optimise BOD removal had little effect on colour removal. This paper provides insight on the nature of recalcitrant organic compounds causing colour formation.

1. Introduction

Historically, the pulp and paper industry has utilised large volumes of fresh water and energy for its processes [1,2]. The wastewaters produced can be highly polluted, with high toxicity and colour, have high biological oxygen demand (BOD) and chemical oxygen demand (COD) and they contain high concentrations of nutrients (nitrogen [N] and phosphorus [P]) and suspended solids [3]. However, stringent international regulations for wastewater discharge from pulp and paper industries have seen an 80–90% reduction in environmental impacts to air and water, and it is expected that these trends will continue [1,2,4].

Pulp and paper wastewaters are generally characterised by low bio-degradability indices (BOD/COD ratio) of typically less than 0.4, due to the presence of toxic components, non-biodegradable compounds and the presence of acclimatized microorganisms, which create an additional challenge for treatment. The difficulty in treating bleached chemithermomechanical pulp (BCTMP), thermomechanical pulp (TMP) and kraft mill effluent (BOD/COD = ~0.4) was demonstrated by MacLean et al. [5] and Rankin et al. [6] using full-scale experiments, and Stephenson et al. [7] and Leiviskä et al. [8] using laboratory investigations. These studies showed that there is a need for advanced pre-treatment prior to discharging effluent to an ASB where biological processes dominate. Thompson et al. [2] indicated that a wastewater treatment process based on a single biological, chemical or physical approach is not effective enough to meet the tightened discharge requirements for the pulp and paper industries. One approach for the treatment of pulp and paper wastewaters is a combination of coagulation and aerated lagoon

---

[*] Corresponding author. Tel.: +61 430467759.
E-mail addresses: dewry001@mymail.unisa.edu.au (R. Lewis), john.vanleeuwen@unisa.edu.au (J.A. van Leeuwen).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.09.089

Nomenclature

ASB	aerated stabilization basins
AMW	apparent molecular weight
BOD_5	five-day biological oxygen demand (mg/L)
BCTMP	bleached chemithermomechanical pulp
CP NMR	cross polarization nuclear magnetic resonance
COD	chemical oxygen demand (mg/L), oxidation with dichromate
C_{obs} values	carbon NMR observabilities
CP-ramp	ramped-amplitude cross polarization
Da	Dalton
HMW	high molecular weight
HPSEC	high performance size exclusion chromatography
HRT	hydraulic retention time
HS	humic substances
KH_2PO_4	potassium dihydrogen phosphate
LMW	low molecular weight
MW	molecular weight
N	nitrogen
$(NH_2)_2CO$	urea
PSS	polystyrene sulfonate
P	phosphorus
TMP	thermomechanical pulp
TN	total nitrogen (mg/L)
TP	total phosphorus (mg/L)
UV	ultraviolet

treatment [9,10]. Coagulation treatment alone can remove high molecular weight (HMW) derivatives of lignin, colour, nutrients and suspended solids, but it does not efficiently remove BOD, COD and low molecular weight (LMW) compounds [1].

The nutrient concentrations in the wastewaters from pulp and paper mills are generally considered limited with respect to the N and P requirements for bacterial growth [11]. Therefore, the stage of the overall process where a coagulation treatment step is implemented becomes an important consideration, particularly where nutrients are required for subsequent biological treatment prior to discharge. Slade et al. [12] found that a conventional BOD:N:P ratio of 100:5:1 is not necessary for low rate treatment options such as ASB. Gill and Ross [13] and Fenske and Gabryel [14] suggested BOD:N:P ratios of 100:2.5:0.5 and 100:3.5:0.7, respectively, are adequate for effective biological treatment. Nutrient addition may be employed to stimulate sufficient microbial activity to degrade toxicants before the wastewater is discharged into receiving environments. In ASBs, potential sources of nutrients are waste stream influents and nutrient recycling from sludge to the overlaying water within the basins, as identified by Slade et al. [12]. However, it is important to note that colour development was not addressed by those authors, which is very difficult to treat.

ASB treatment processes have been found to be ineffective for decolourization of pulp and paper mill wastewater. Milestone et al. [15] reported that from 19 pulp and paper mills surveyed, ASB treatment led to an average increase in colour of 20–40%. The blackish or brownish colour of the effluent is mainly attributed to complex compounds derived from polymerization between lignin, carbohydrate and extractive degraded products and tannin produced during various pulping/bleaching operations [1,4,16]. This colour is not only aesthetically undesirable but also inhibits the natural processes of photosynthesis due to the absorbance of sunlight.

Lignocelluloses are the major component of plant biomass and consist of three types of polymers, namely cellulose, hemicelluloses and lignin [17]. Their insolubility, with HMW of 1000–10,000 Dalton (Da), makes these compounds difficult to degrade naturally and results in a significant increase in colour of the treated wastewater [4]. The resistance of lignin and its derivatives to biological degradation has been attributed to the presence of double bonds conjugated with aromatic rings of lignin, aromatic carbon, quinone methides and quinone groups within the wastewater [17].

Humic substances (HS), which have similar HMW (>1000 Da) compounds as derivatives of lignin, are produced through humification processes by biological activity. The production of HS also contributes to colour development through decomposition of lignin, proteins, pectins, polysaccharides and tannin [18]. These HS produce a ^{13}C cross polarization nuclear magnetic resonance (^{13}C CP NMR) spectroscopic characteristic resembling lignin derived compounds [16].

The ultimate aim of this study was to investigate the change in the character of organics remaining in the treated effluent from a *Pinus radiata* sulfite pulp and paper mill following alum treatment in a simulated laboratory scale ASB process. Previous investigations demonstrated that successful manipulation of the BOD:N:P ratio can reduce BOD to low levels [19]. However, the formation of colour was not addressed. A particular emphasis in this study focused on the changes in the character of organic compounds which contribute to the formation of colour in the simulated ASB treatment using the coagulated wastewater where bio-available nitrogen and phosphorous were limited.

2. Materials and methods

2.1. Wastewater and sludge sources

Wastewater and sludge samples were sourced from a pulp and paper mill in South Australia. The pulp mill produces a peroxide bleached pulp, utilising *Pinus radiata* plantation soft wood. The total combined volume of wastewater produced from the *Pinus radiata* sulfite pulp mill mixed with wastewaters from an adjacent paper manufacturing mill is ∼30 ML per day. The combined wastewaters are currently treated by primary clarification followed by an ASB (3 lagoons in series, with the first two lagoons aerated), with 26–30 days hydraulic retention time (HRT). The three lagoons are, in sequence, a continuously stirred tank reactor, a plug-flow reactor and a maturation pond.

One batch of raw wastewater and two batches of coagulated wastewater were obtained using a pilot plant (∼250 L/h in a 500 L settling clarifier) that was sited at the pulp mill. Coagulation was performed using 80 ppm of $Al_2(SO_4)_3 \cdot 18H_2O$ as Al^{3+} (1860 ppm of alum). The selection of alum dose was based on maximizing the removal of colour and TP.

Comparison of raw and coagulated wastewater (Batch #1) after pH adjustment to 6.5 ± 0.5 (Table 1) showed that coagulation treatment using 1860 mg/L of alum was effective in reducing $colour_{456nm}$, $UV_{254\ and\ 280nm}$, (∼80%) but less effective in reducing COD (∼70%). As the pulping process and wastewaters are consistent, only the raw wastewater of Batch #1 was analysed and reported below for comparison with coagulated wastewaters. As similarly found by Chow et al. [20], the qualities of post-coagulated wastewaters (treated with the same alum dose) showed comparable qualities (Table 1).

2.2. ASB – laboratory scale simulations

2.2.1. Tank dimensions

Two identical laboratory-scale ASBs each consisting of three tanks (Fig. 1) were operated in parallel. For each ASB, Tank 1 (8.5 L) was made of PVC while Tank 2 (5.6 L) and Tank 3 (8.6 L) were made of mild steel coated with an anticorrosive paint. Tank 2 was divided