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Diagnosis of dissolved organic matter removal by GAC treatment in biologically treated papermill effluents using advanced organic characterisation techniques

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ABSTRACT

Granular activated carbon (GAC) exhaustion rates on pulp and paper effluent from South East Australia were found to be a factor of three higher (3.62 cf. 1.47 kg m^{-3}) on Kraft mills compared to mills using Thermomechanical pulping supplemented by Recycled Fibre (TMP/RCF). Biological waste treatment at both mills resulted in a final effluent COD of 240 mg L^{-1}. The dissolved organic carbon (DOC) was only 1.2 times higher in the Kraft effluent (70 vs. 58 mg L^{-1}), however, GAC treatment of Kraft and TMP/RCF effluent was largely different on the DOC persisted after biological treatment. The molecular mass (636 vs. 534 g mol^{-1}) and aromaticity (5.35 vs. 4.67 L mg^{-1} m^{-1}) of humic substances (HS) were slightly higher in the Kraft effluent. The HS aromaticity was decreased by a factor of 1.0 L mg^{-1} m^{-1} in both Kraft and TMP/RCF effluent. The molecular mass of the Kraft effluent increased by 50 g mol^{-1} while the molecular mass of the TMP/RCF effluent was essentially unchanged after GAC treatment; the DOC removal efficiency of the GAC on Kraft effluent was biased towards the low molecular weight humic compounds. The rapid adsorption of this fraction, coupled with the slightly higher aromaticity of the humic components resulted in early breakthrough on the Kraft effluent. Fluorescence excitation–emission matrix analysis of the each GAC treated effluent indicated that the refractory components were higher molecular weight humics on the Kraft effluent and protein-like compounds on the TMP/RCF effluent. Although the GAC exhaustion rates are too high for an effective DOC removal option for biologically treated pulp and paper mill effluents, the study indicates that advanced organic characterisation techniques can be used to diagnose GAC performance on complex effluents with comparable bulk DOC and COD loads.

1. Introduction

Pulp and paper mill effluent is one of the most challenging industrial effluents to treat and reuse due to the complexity of residual natural organics matter from the wood pulp and the inorganic and synthetic chemicals added during the papermaking process (Suntio et al., 1988). Notwithstanding this, the implementation of best water management practices in paper production, modern mills are increasingly deploying external recycling via end-of-pipe treatment to minimise demand on surface water supplies, particularly in drought prone countries such as Australia (Richardson et al., 2008; Hodgkinson et al., 2009; Negaresh et al., in press). Biological treatment of commingled mill effluent using suspended or attached growth is sufficient for reuse however, the persistence of refractory organics limits reuse opportunities in paper production without further processing (Stephenson and Duff, 1996; Amat et al., 2005; Temmink and Grolle, 2005; Catalkaya and Kargi, 2007; Ciputra et al., 2010).

A suite of tertiary treatment technologies can be used to remove refractory organics options including coagulation, adsorption, ion exchange, oxidation and membrane filtration (Thompson et al., 2001; Mänttäri et al., 2002; Pokhrel and Viraraghavan, 2004; Mänttäri et al., 2006). In each case, the efficiency of the treatment process depends on the concentration and nature of dissolved organic matter (DOM). Consequently, selection and design of appropriate tertiary treatment needs an understanding of the quality and quantity of DOM. Adsorptive and exchange processes such as granular activated carbon (GAC) are most sensitive to the aromaticity

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and molecular weight of the refractory organics; coagulation and oxidation are influenced by DOM concentration (Zhang and Chuang, 2001; Temmink and Grolle, 2005) and membrane filtration depends on the distribution of molecular weight, charge and hydrophobicity (Bellona et al., 2004). DOM removal using GAC is reported in the past for wastewater effluents (Gur-Reznik et al., 2008; Kim et al., 2009) and reverse osmosis concentrates with DOC as high as 38 mg L^{-1} (Dialynas et al., 2008; Philibert et al., 2011).

Of particular importance is the impact of various molecular weight fractions of the DOM that persists after biological treatment on the separation process. Moreover, the relative and overall abundance of these fractions in the secondary treated effluent will differ depending on the use of the Kraft, Thermomechanical (TMP) or Recycled Fibre (RCF) method in the pulping process (Smook, 1992; Thompson et al., 2001). The Kraft process is a chemically assisted process for turning wood into pulp. It removes most of the lignin from the wood, leading to a brighter, stronger paper with uses such as copy paper, tissue paper and packaging. The TMP process uses mechanical energy and elevated temperature to turn wood into pulp, whilst the RCF process uses chemicals to separate and float off any ink attached to fibres. The TMP coupled with RCF process create a pulp with shorter fibres and a higher organic content, leading to a weaker paper suitable for use in newsprint and paperboard. This process has a water usage of around 9–10 $m^3\ t^{-1}$ and produces a less concentrated effluent (Richardson et al., 2008).

To date, characterisation of the DOM in pulp and paper mill effluent is generally represented through surrogates such as colour, COD, BOD, dissolved organic carbon (DOC) and UV_{280} (Pokhrel and Viraraghavan, 2004; Temmink and Grolle, 2005). These conventional surrogate parameters provide a gauge of total organic loading but have limited information of the molecular composition. The selection of treatment option and design parameters are by and large based on these conventional surrogates, which fails to detail the molecular nature of DOM making it difficult to gain insight into the efficiency and performances of the recycling processes. Therefore systematic characterisation of bulk water can provide better understanding of their fate, transport and impact during water treatment and reuse (Sharma et al., 2011). Advanced characterisation of organics based on molecular weight and fluorogenic origin is gaining interest in water treatment sector (Hudson et al., 2007; Peiris et al., 2010; Huber et al., 2011; Sharma et al., 2011). However use of advanced organic characterisation techniques for paper mill effluents is limited (Ciputra et al., 2010; Henderson et al., 2011).

The purpose of this paper is to have advanced organic characterisation techniques to explain the difference in treatability of wastewater effluent using a water matrix possessing high organic loading. This paper highlights the potential for coupling rapid small scale column test (RSSCT) with size exclusion chromatography–organic carbon and nitrogen detector (LC–OCND) and fluorescence spectroscopy to compare the molecular weight and fluorogenic origin of the DOM fractions to discriminate between the performance of GAC on biologically treated Kraft and TMP/RCF mill effluent. The treatability difference between the two effluents is discussed in terms of various DOM characterisation methods.

2. Theoretical approach-RSSCT

The adsorption efficiency of GAC can be rapidly assessed by RSSCT, a scaled down version of pilot column testing, that is less expensive and time-consuming than full-scale column studies (ASTM, 2003; Sperlich et al., 2005). RSSCT uses empty bed contact time (EBCT) and hydraulic loading to describe the adsorption process. In order to simulate the pilot scale column in RSSCT, hydrodynamics and mass transport parameters like GAC particle size, EBCT, and hydraulic load are scaled down using dimensionless mathematical parameters based upon a mass transfer model, known as the dispersed-flow pore surface diffusion model. Crittenden used this technique to simulate the removal of organic micro pollutant and natural organic matter by GAC in a full-scale column (Crittenden et al., 1986,1987,1991). Full-scale column scaling parameters can be determined using a constant diffusivity (CD) or proportional diffusivity (PD) model. The two approaches differ in terms of surface diffusivity, which is the rate by which intra particle diffusion is limited. Surface diffusivity is assumed to be independent of the particle size for the CD approach and linearly dependent for the PD approach. The relationship for EBCT and particle between the RSSCT and the full scale column is determined by Eq. (1):

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^{2-X} \quad (1)$$

where $EBCT_{SC}$ and $EBCT_{LC}$ are the EBCT for small and large scale column tests, R_{SC} and R_{LC} are the particle radius for the small and large scale column tests and X is the diffusivity factor. For CD and PD approaches, the value of X is 0 and 1 respectively.

Among the two approaches, a most suitable design criterion for a specific experimental condition depends on the nature and molecular structure of the adsorbate. The CD design approach is appropriate for external mass transfer limited adsorption, i.e. for small molecular weight organics like synthetic organic carbons. The PD design approach is considered valid for intra particle mass transfer limited organics removal, i.e. for large molecular weight organics like natural organic matter (Matsui et al., 1994; Summers et al., 1994). Therefore, a PD design approach was adopted as the molecular weight of the humic substances (HS) in the mill effluent was of a comparable range to the International Humic Substances Society (IHSS) standards, derived from fresh waters (Ciputra et al., 2010).

3. Methods and materials

3.1. Effluent source

Biologically treated Kraft and TMP/RCF effluent was collected from paper mills located in Gippsland, Victoria and Albury, New South Wales respectively and stored at 4 °C. In each case the effluent had received biological treatment followed by membrane filtration (Richardson et al., 2008; Hodgkinson et al., 2009). Detailed water quality analysis is presented in Table 1.

3.2. Granular activated carbon

ACTICARB BAC-GS1300 (Activated Carbon Technologies, Australia), coal based and steam activated carbon was used in this study.

Table 1
Water quality parameters measured for the Kraft and TMP/RCF mill effluents.

Parameter	Kraft	TMP/RCF
pH	7.8	7.9
Colour (PCU)	1070	372
Total dissolved solids (mg L^{-1})	2680	1430
DOC (mg L^{-1})	70	57
COD (mg L^{-1})	240	240
Calcium (mg L^{-1})	148	124
Sodium (mg L^{-1})	776	259
Alkalinity (mg L^{-1})	364	423
Sulphate (mg L^{-1})	947	420
Chloride (mg L^{-1})	493	43