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Evaluation of ion exchange resins for the removal of dissolved organic matter from biologically treated paper mill effluent

Mojgan Bassandeh [a], Alice Antony [a], Pierre Le-Clech [a], Desmond Richardson [b], Greg Leslie [a,*]

[a] UNESCO Centre for Membrane Science and Technology, The University of New South Wales, Sydney 2052, Australia
[b] Technical Support & Development, Norske Skog Paper Mills (Australia) Ltd., Boyer, Tasmania 7140, Australia

HIGHLIGHTS

- TAN1 anion exchange resin exhibited effective removal efficiency of organics.
- Action of anion exchange resins on organics was both by exchange and adsorption.
- Anion exchange resins effectively removed the aromatic component of organics.

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ABSTRACT

In this study, the efficiency of six ion exchange resins to reduce the dissolved organic matter (DOM) from a biologically treated newsprint mill effluent was evaluated and the dominant removal mechanism of residual organics was established using advanced organic characterisations techniques. Among the resins screened, TAN1 possessed favourable Freundlich parameters, high resin capacity and solute affinity, closely followed by Marathon MSA and Marathon WBA. The removal efficiency of colour and lignin residuals was generally good for the anion exchange resins, greater than 50% and 75% respectively. In terms of the DOM fractions removal measured through liquid chromatography–organic carbon and nitrogen detector (LC–OCND), the resins mainly targeted the removal of humic and fulvic acids of molecular weight ranging between 500 and 1000 g mol^{-1}, the portion expected to contribute the most to the aromaticity of the effluent. For the anion exchange resins, physical adsorption operated along with ion exchange mechanism assisting to remove neutral and transphilic acid fractions of DOM. The column studies confirmed TAN1 being the best of those screened, exhibited the longest mass transfer zone and maximum treatable volume of effluent. The treatable effluent volume with 50% reduction in dissolved organic carbon (DOC) was 4.8 L for TAN1 followed by Marathon MSA – 3.6 L, Marathon 11 – 2.0 L, 21K-XLT – 1.5 L and Marathon WBA – 1.2 L. The cation exchange resin G26 was not effective in DOM removal as the maximum DOC removal obtained was only 27%. The resin capacity could not be completely restored for any of the resins; however, a maximum restoration up to 74% and 93% was achieved for TAN1 and Marathon WBA resins. While this feasibility study indicates the potential option of using ion exchange resins for the reclamation of paper mill effluent, the need for improving the regeneration protocols to restore the resin efficiency is also identified. Similarly, care should be taken while employing LC–OCND for characterising resin-treated effluents, as the resin degradation is expected to contribute some organic carbon moieties misleading the actual performance of resin.

1. Introduction

Anion exchange resins have been used to remove dissolved organic matter (DOM) from surface water in order to reduce the formation of disinfection by product precursors (Boyer and Singer, 2005; Tan and Kilduff, 2007; Cornelissen et al., 2008). Similarly, ion exchange resins have also been employed for DOM removal from ground water and wastewater (Brattebø et al., 1987). In recent years, there is growing interest in using ion exchange resins in paper mills and cardboard industries for the reduction of colour contributing DOM fractions from mill effluent (Bourke and Holmquist, 2009; Richardson et al., 2010). These studies focused on using magnetic ion exchange resin for the removal of DOM and the results indicated the potential application of this resin for the reclamation and reuse of water discharged from pulp and paper mills.

* Corresponding author. Tel.: +61 2 93856092.
E-mail address: g.leslie@unsw.edu.au (G. Leslie).

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In-mill reuse of pulp effluent for boiler make up and steam generation depends on the removal of both salt and colour, while removal of organics is important for reuse in pulp bleaching and chemical makeup applications. Studies on the use of commercial ion exchange resins for DOM removal in pulp and paper mill effluent are limited. An evaluation of treatment options for Kraft mill effluent found that the adsorption of organic pollutants by ion exchange resin was promising compared to activated carbon treatment (Zhang and Chuang, 2001). A comparative assessment of the performance of carbon, resin and membranes on biologically treated effluent from thermomechanical and Kraft mills found that while ion exchange removed more DOM than carbon, the resin could not retain the low molecular weight neutral fraction that were readily removed by nanofiltration membranes (Ciputra et al., 2010). In theory, ion exchange is a potential alternative to nanofiltration which has been identified as the preferred final step for In-mill effluent reuse schemes. Ion exchange resins can be tailored to remove mono and divalent salts as well as organics. Like membrane filtration, the resin beds are modular and have a small footprint. Moreover, regeneration can be achieved using common acids and bases and unlike membrane filtration the process does not require the high pressure pumps, variable speed drives and the attendant control systems. However, more work is required to identify resins that can remove both charged and uncharged organics to achieve the broad spectrum salt and organic separation performance of membrane filtration.The removal efficiency of natural organic matter using commercial ion exchange resins was studied in the past mainly through measuring water quality parameters like colour, dissolved organic carbon (DOC) and UV absorbance at 254 nm (Croue et al., 1999; Bolto et al., 2002; Humbert et al., 2005; Tan et al., 2005); some studies investigated the selectivity of the resins concentration using advanced organic characterisations studies (Tan and Kilduff, 2007; Cornelissen et al., 2008). While these studies offer useful guidance in understanding the removal of DOM fractions in general, this cannot be directly applied for the paper mill effluent, given the complex nature of these types of effluent. Paper mill effluent is a complex mixture of acids, phenolic compounds, sugars and inorganic substances derived from the wood pulp and the chemical additives used during the processing (Suntio et al., 1988). A dark colour to the effluent is expected to be imparted by wood derivatives, lignins and/or polymerised tannins (Crooks and Sikes, 1990). Degradation products of lignin and its derivatives possess strong linkages within the molecule and therefore their biological/chemical degradation remains difficult (Zhang and Chuang, 2001). Therefore, removal of these DOM components needs an efficient sorbent surface capable of acting on the lignin and tannin moieties.

The aim of the present study is to evaluate a suite of ion exchange resins of different exchange behaviours to remove various DOM fractions from paper mill effluent and to gain insight into the dominant mechanism of DOM removal using advanced organic characterisation techniques like liquid chromatography–organic carbon and nitrogen detector (LC–OCND), fluorescent excitation emission matrix (FEEM) and rapid resin fractionation (RRF) A detailed understanding of the DOM removal mechanism assists designing complex water recycling systems and reuse. The ion exchange resins were selected to cover weak and strong anion exchange resins in comparison with a cation exchange resin. This study includes a resin not reported so far, DOWEX TAN1, which is suggested to be effective for water containing wood extractives like tannins (DOWEX, 2012). The performance of the resins and regeneration capacity were also studied in dynamic mode through column studies.

2. Materials and methods

2.1. Effluent source

Paper mill effluent for the present study was sourced from Norske Skog Paper Mills (Australia) Ltd., NSW, newsprint plant using thermomechanical pulping (TMP) and recycled fibres (RCF). 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 the RCF process creates a pulp suitable for use in newsprint. The effluent was collected after the biological treatment at the end-of-pipe followed by microfiltration using Polyvilylidenedifluoride membrane module (Pall USV-3003) of 0.2 μm pore size at a constant pressure of 1.5 bar. The filtered effluent was stored below 4 °C until commencing the experiments. A detailed water quality analysis of the effluent collected is presented in Table S1.

2.2. Ion exchange resins and regeneration chemicals

The ion exchange resins used in this study are listed in Table S2 along with the manufacturer specifications for type, backbone matrix, exchange capacity, water content, functional group and mean particle size. The resins were conditioned by soaking in methanol for 8 h and rinsing with milliQ water. The exhausted resins were regenerated according to the manufacturer recommendations; AR grades of NaOH, HCl and NaCl were used for regeneration.

2.3. Analytical methods

The water quality of the untreated and treated effluents was measured and characterized through various techniques. The DOC was measured with a TOC-5000A analyser (Shimadzu, Australia) using the non-purgeable organic carbon (NPOC) method. Specific cation concentrations were determined by inductively coupled plasma–optical emission spectroscopy (Perkin Elmer Optima 3000 DV 3000, USA). The apparent colour was measured from specific absorbance at 455 nm (Clesceri et al., 1998). The lignin residuals present was measured from the UV absorbance at 280 nm (Mänttäri et al., 1997).

The DOM of the samples before and after anion exchange resin treatment was characterized into three fractions based on their hydrophobicity by RRF as detailed elsewhere (Ciputra et al., 2010). Briefly, the effluent sample was adjusted to pH 2 and passed onto DAX-8 and XAD-4 macroporous resin packed columns to adsorb hydrophobic acid (HPhoA) and transphilic acid (TPhiA) fractions respectively. The unabsorbed DOM fraction after two columns was characterized as hydrophilic compounds (HPhi). The DOC of the fractions before entering the resin column and after successive resin column outlets was measured to determine the individual organic fractions.

Further characterisation of DOM for its molecularity and fluorogenic origin was performed using LC–OCND (Henderson et al., 2011; Huber et al., 2011; Neale et al., 2011). A LC–OCND system, model 8 (DOC Labor, Dr. Huber, Germany) working based on the Gräntzel thin film reactor, using Toyopearl HW–50S weak cation exchange gel filtration column (Huber et al., 2011). In LC–OCND, the fractionation is based on steric interaction over a wide range of molecular weights and detected and quantified using three inline detectors; an organic carbon detector (OCD), ultraviolet absorbance detector (UVD) and organic nitrogen detector (OND). 1000 μL of the diluted samples were eluted with phosphate buffer (28 mM of phosphate buffer, pH 6.6) at a flow rate of 1.1 mL min^{-1}.

LC–OCND analysis provides the molecular weight distribution of the sample through size exclusion chromatography using