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Monitoring reverse osmosis performance: Conductivity versus fluorescence excitation–emission matrix (EEM)

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ABSTRACT

This paper evaluated dissolved organic matter (DOM) rejection by reverse osmosis (RO) membranes employed in full-scale water reclamation plants with two techniques based on fluorescence to assess its suitability as a novel method for verification of membrane process integrity. Excitation–emission matrices (EEM) of feed and permeate samples from individual pressure vessels, complete stages and RO trains of two full scale plants were analysed with a fluorescence regional integration technique. Depending on the excitation–emission region quantified, DOM rejection up to around 99.5% was regularly measured and fluorescence measurements could be used as more sensitive tool compared to conductivity profiling when assessing membrane installations. A blue-shift in the fluorescence of the humic substances peak was observed and could be explained by determining size distribution of organic matter by size exclusion chromatography (SEC) with fluorescence detection. The results demonstrated that the size distribution of fluorescent DOM changed towards lower molecular weight from feed to permeate due to increased rejection of high molecular weight compounds. Preliminary trials showed rejection of high molecular weight substances and consequentially membrane integrity beyond 99.9%. We conclude that fluorescence coupled with regional integration techniques and potentially SEC is a promising sensitive technique to assess RO membrane integrity.

1. Introduction

Water recycling has become an accepted solution to augment water supplies and overcome water scarcity due to changes in rainfall patterns and population increases [1]. Membrane technology is widely used to generate recycled water that is fit-for-purpose, as it ensures high water quality and minimise the risk to public health [2]. Around the world, a number of advanced water treatment plants (AWTPs) have been constructed to purify secondary effluent from wastewater treatment plants by microfiltration (MF) or ultrafiltration (UF), reverse osmosis (RO), advanced oxidation process (AOP) and post-chlorination. Together, these barriers are designed to prevent the infiltration of chemical and microbial contaminants from wastewater into drinking water supplies [3].

RO membranes are commonly used in tertiary treatment for water reuse applications and sea or brackish water desalination as a physical disinfection process besides their capacity to remove salt and other inorganic and organic contaminants. For validation and operational monitoring, the RO process must be continuously monitored to ensure their correct operation to prove the log rejection that they have been validated for. Log rejection is a way to express the removal efficiency for a specific target (e.g. organism, particulate or surrogate) [4]. To monitor the integrity of RO membranes and continuously assess their rejection performance, on-line conductivity and total organic carbon (TOC) measurement are generally used to measure performance of critical control points (CCPs) [5,6]. CCPs are validated preventive measures (such as the reverse osmosis process) associated with removal of a target criteria (such as viruses). The performance of CCPs (as sometimes expressed by "log-removal") can be validated by once-off challenge test using the target contaminant (such as a virus or virus-like particle), and this performance is then related to a setpoint for the operational performance measure (usually conductivity) that can be measured online. This operational performance setpoint is referred to as the critical limit for the process, which needs to be maintained to eliminate or reduce high

Abbreviations: AWTP, Advanced water treatment plant; CCP, Critical control point; EEM, Excitation emission matrix; FRI, Fluorescence regional integration; MW, Molecular weight; PV, Pressure vessel; SEC, Size exclusion chromatography; SEQ, South East Queensland

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risks to acceptable levels [7]. Conductivity is a good surrogate measurement for rejection of ions by the membrane, which is typically 98–99%. A major disadvantage is that rejection of conductivity tends to underestimate the performance of RO membranes with regards to the rejection of micro-organisms including viruses [8]. On-line TOC monitoring has shown to be a better measure of the rejection of micro-organisms than on-line conductivity (99.5–99.9%) [9]. Nowadays, for full scale RO plants rhodamine-WT is used during initial plant validation and on-line conductivity, TOC and sulphate measurement are used for operational monitoring of integrity. MS2 bacteriophage (or MS2 phage) is generally used in challenge tests as virus surrogate and has been reported as the best available process indicator due to its small size and shape (similar to poliovirus), negative charge in water at circumneutral pH, ease of use in laboratory and above all its non-hazardous nature to humans [10–12]. However, its use at large scale and on-line quantification is not possible with current analytical techniques and off-line its frequent measurement is costly.

To improve sensitivity and selectivity, Henderson et al. [13] suggested the analysis of fluorescent dissolved organic matter (DOM) as a potential surrogate due to its chemical properties. DOM is a heterogeneous mixture of aromatic and aliphatic hydrocarbon structures containing different functional groups. Its composition and concentration in aquatic samples are highly variable and depend on the water source [14,15]. Analysis of DOM provides a good indication of water quality. For this reason, the use of Excitation Emission Matrix (EEM) fluorescence to analyse DOM in membrane organic fouling studies, to differentiate the water quality in the steps of recycled water treatment plants and to identify cross-connections in dual pipe distribution systems has recently gained a lot of attention [16–20]. Different techniques can be applied to interpret EEM fluorescence data such as fluorescence regional integration (FRI) [14], chemometric techniques as the parallel factor analysis (PARAFAC) [21,22] or principal component analysis (PCA) [18]. In 2009, Singh et al. [19] showed that DOM in RO permeates can be characterized by EEM fluorescence allowing differentiation of the permeate quality among different stages of the RO trains. They also demonstrated that humic-like fluorescence can be detected sensitively in this matrix.

In the present study we propose to use DOM removal analysed by EEM fluorescence coupled to a FRI technique as a tool to monitor RO membrane integrity, which to the authors' best knowledge has not been published before. Feed and permeate waters from different pressure vessels (PV) in a RO train were analysed by conductivity and EEM fluorescence to analyse the variability of ion and DOM rejection. A FRI technique from fluorescence spectroscopy was used to calculate the area of three delimited regions (noted region I, II and III) in two full scale AWTPs. In addition to the direct measurement of the samples by fluorescence EEM, size exclusion chromatography (SEC) with fluorescence detection was used to further characterize the DOM in feed and permeate samples.

The objectives of this work are (i) to assess performance variability within RO trains and AWTPs as measured by conductivity and DOM rejection; (ii) to evaluate EEM fluorescence and SEC with fluorescence detection as a monitoring tool for DOM rejection by RO membranes with high sensitivity, which could potentially be used as virus surrogate for RO process validation and operational monitoring.

2. Material and methods

2.1. Site descriptions and samples

Samples were collected from the RO process of two AWTPs in South East Queensland (SEQ) over a period of 18 months from September 2010 to February 2012 (Fig. 1). In plant A, 7 PVs in stage 1, 4 PVs in stage 2 and 2 PVs in stage 3 have been sampled 7 times in 5 campaigns; in plant B, 3 PVs in stage 1, 10 PVs in stage 2 and 8 PVs in stage 3 have been sampled 5 times in 4 campaigns. When different trains have been sampled on the same day, water quality for the combined feed and permeate of the RO process has been determined only once. Both RO processes are operated at 85% of recovery throughout three stages, use two different RO thin-film composite polyamide membranes and are fed by secondary effluent from biological nutrient removal plants pre-treated by ferric iron coagulation, clarification and ultrafiltration.

All samples were collected in 100 mL amber glass bottles, transported in cold storage and analysed within three days. The water quality of the RO feed and permeate for the sampling period is detailed in Table 1.

2.2. Fluorescence analysis

Fluorescence measurements of DOM were performed using a PerkinElmer LS-55 luminescence spectrometer (PerkinElmer, Australia) in a 1 cm quartz cuvette operated with the Winlab® software provided by PerkinElmer. Fluorescence intensity was recorded varying excitation wavelengths from 200 nm to 400 nm at steps of 5 nm, and emission wavelengths from 280 nm to

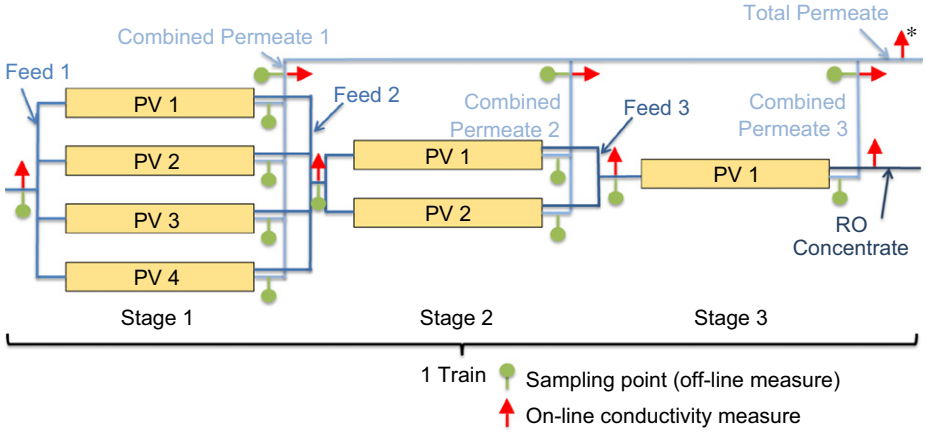

Fig. 1. (Color online) Simplified schematic of an RO train in plant A with on-line conductivity sensors (red triangle) and sampling points used to measure off-line conductivity and fluorescence (green circle). *In plant B, the total permeate conductivity is monitored on-line for entire RO trains.