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Chemical characterization by gas chromatography-mass spectrometry and inductively coupled plasma-optical emission spectroscopy of membrane permeates from an industrial dairy ingredient production used as process water

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ABSTRACT

Reusing reverse osmosis (RO) membrane permeate instead of potable water in the dairy industry is a very appealing tactic. However, to ensure safe use, the quality of reclaimed water must be guaranteed. To do this, qualitative and quantitative information about which compounds permeate the membranes must be established. In the present study, we provide a detailed characterization of ultrafiltration, RO, and RO polisher (ROP) permeate with regard to organic and inorganic compounds. Results indicate that smaller molecules and elements (such as phosphate, but mainly urea and boron) pass the membrane, and a small set of larger molecules (long-chain fatty acids, glycerol-phosphate, and glutamic acid) are found as well, though in minute concentrations (<0.2 μ*M*). Growth experiments with 2 urease-positive microorganisms, isolated from RO permeate, showed that the nutrient content in the ROP permeate supports limited growth of 1 of the 2 isolates, indicating that the ROP permeate may not be guaranteed to be stable during protracted storage.
Key words: dairy ingredient production, process water, membrane filtration, quality characterization

INTRODUCTION

Reducing the overall water footprint has become an important objective in the dairy processing industry due to increasing cost of discharge and intake as well as limited availability of potable water. The potable water consumption can be greatly reduced through efficient use of process waters, such as membrane permeate and evaporator condensate, in different areas of the production including cleaning processes.

In dairy processing facilities, membrane filtration technologies are already frequently used to create new products. These technologies can be characterized by their ability to separate molecules and constituents of different sizes. At Arla Foods Ingredients, Viby, Denmark, whey, a by-product from cheese production facilities, is processed into new products. First, UF membranes are used to retain whey proteins, and the permeate is processed through a 2-stage reverse osmosis (**RO** plus RO polisher; **ROP**) membrane plant to collect lactose. The collected whey proteins are used downstream to produce various products and constituents, whereas the lactose is used as a food ingredient (e.g., in infant formula). The focus of this investigation is the use potential of the ROP permeate as a process water stream.

Although use of process water is an attractive option, microbiological safety is of major importance in the food and dairy industry and must be ensured at all times. To do this, real-time online monitoring of relevant parameters should be considered (Casani et al., 2005). Process analytical technology provides the principles for real-time online monitoring (van den Berg et al., 2013), but to select the appropriate measurement technique the target molecule(s) must first be identified. The RO(P) permeates from dairy-derived water have been reported to have a very low organic load and low conductivity indicating minimal concentrations of organic compounds and minerals. Organic load has traditionally been expressed by classical, cumulative numbers such as total organic carbon, chemical oxygen demand, and total nitrogen (Vourch et al., 2005, 2008). However, these cumulative measurements do not provide insight into which specific compounds permeate the membranes. Vourch et al. (2008) looked at selected

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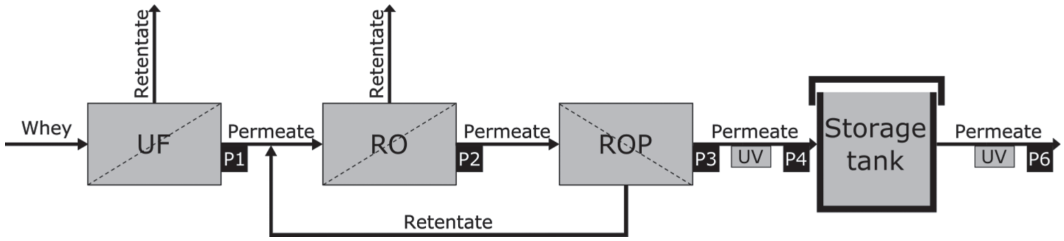

Figure 1. Schematic overview of UF processing and reverse osmosis (RO) plus RO polisher (ROP) lactose and water recovery plus storage. The process water sampling points are marked P1 to P6.

organic compounds and ions in membrane permeates and vapor condensates. A different approach is taken (e.g., in the field of metabolomics) where analytical techniques for the characterization of complex mixture samples have been developed. Through derivatization of functional groups with a labile proton using (e.g., trimethylsilyl), classes of compounds previously unsuitable for GC analysis become volatile and can be detected using fully automated sample preparation and analysis workflows (Khakimov et al., 2013). These analytical techniques open up for a 2-stage data analysis approach in the same analytical run: exploratory untargeted (unbiased) data analysis followed by a targeted analysis of a selection of compounds using a large sample set. These very low concentration compounds can be determined via a combination of automated sample pretreatment, GC, sensitive MS, and advanced data analysis. Regarding element analysis, inductively coupled plasma with optical emission spectroscopy (**ICP-OES**) has become more popular in recent years, providing a high-throughput, broad (unbiased) coverage both in terms of elements and concentration ranges (Hansen et al., 2009; Husted et al., 2011).

In the present study we characterize the chemical composition of UF, RO, ROP permeate, and storage tank water in a dairy ingredient production through untargeted derivatization based GC-MS coupled with advanced chemometric analysis. A selection of the chemical compounds are quantified via calibration standard series. Furthermore, detailed element composition of the streams is determined over a 10-h production run through ICP-OES analysis to investigate the dynamic behavior of element retention. This information was supplemented with 6-d growth experiments (radically surpassing normal process water storage) performed with 2 microorganisms isolated from RO permeate, a *Pseudomonas* sp. and a *Staphylococcus* sp., to test if the low nutrient levels in the ROP permeate were sufficient to support microbial growth. To the best of our knowledge this is the first study performed for an untargeted chemical characterization and element analysis of dairy membrane permeates.

MATERIALS AND METHODS

Samples Collected

All samples were collected at the Arla Foods Ingredients production facilities (Nr. Vium, Denmark) in 250-mL amber, sterile, polypropylene sample bottles (Isolab, Wertheim, Germany) over a sample collection period of less than 1 min, and stored at 5°C until analysis. Immediately before sampling, the process valves were opened and flushed to waste for approximately 10 s. Conductivity was measured on site, directly after collection, and before analysis for quality assurance purposes. A schematic illustration of the process and sampling locations is presented in Figure 1. Samples are denoted as follows: P1, UF permeate; P2, RO permeate; P3, ROP permeate before UV treatment (400 J/m^2, BX100e, Wedeco, USA); P4, ROP permeate after UV; P6, ROP permeate after storage tank, and UV treatment.

Process water samples for GC-MS analysis were collected 3 or 4 times on the same day and analyzed in duplicate or triplicate for P1, P2, P3, P4, and P6, leading to 15 samples overall (and 46 analysis runs in total). Process water samples for ICP-OES were collected simultaneously from UF, RO, and ROP permeate (P1, P2, and P4, respectively; 40 × 3 permeate samples; for further details, see Skou et al., 2017a). Sampling was initiated immediately after the treatment plant was started (following a cleaning in place) and continued for approximately 10 h. This time period included 2 feed tank changes where samples were collected with a higher frequency, accompanied by a lower sampling frequency in between.

The 2-stage RO+ROP plant consists of the RO section with 9 loops in parallel each with 6 membrane elements in series and the ROP segment of 4 loops in parallel each with 6 membrane elements in series; all elements are DOW Hypershell RO-8038 (TetraPak, Silkeborg, Denmark). The feed to the RO+ROP plant is UF permeate from whey processing adjusted to pH 5.8 with a flow ranging from 100 to 150 $m^3 \cdot h^{-1}$, target