Evaluation of fouling and RO performance for MBR treated fruit wastewater
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ABSTRACT
Fruit processing facilities are looking for ways to reduce water consumption to counter the impact of climate change. A good alternative is an MBR system to treat the processing wastewater, followed by tertiary treatment using a reverse osmosis (RO) unit to enable water reuse. However, fouling of the RO membrane causes operational challenges. As a result, experiments were completed on treated fruit processing wastewater to identify the causes of fouling that originated from the MBR effluent and develop best management practices (BMPs) to minimize fouling of the RO membrane. Physical and chemical analyses along with visual inspection of the membrane surface using scanning electron microscopy (SEM), energy diffusive X-ray (EDX) and Fourier transform infrared (FTIR) spectroscopy were completed. The issue of RO membrane fouling and subsequent flux decline was directly related to the presence of soluble microbial products, specifically dissolved organic matter (DOM) in the MBR effluent. The developed BMPs show that the previously completed enhanced coagulation-GAC sorption process, when combined with an online non-chemical flushing regimen and proper membrane preservation, keeps the flux readings high, resolving frequent fouling and cleaning problems of the RO membrane.

Key words | enhanced coagulation-GAC sorption, fouling, fruit wastewater, on-line cleaning protocols, reverse osmosis

HIGHLIGHTS
- Identified causes of fouling on a RO membrane post MBR treatment.
- Fouling and subsequent flux decline due to presence of soluble microbial products in MBR effluent.
- Treatment of MBR effluent can reduce fouling tendencies.
- Developed an on-line cleaning process to minimize fouling of RO membrane.

INTRODUCTION
Reverse osmosis (RO) is a pressure-driven membrane process that is widely recognized as the leading technology for critical water treatments including seawater desalination (Wenten & Khoiruddin 2016) and various industrial wastewaters (Mölter & Lindenthal 1995; Suárez et al. 2014). In addition to desalination, RO can produce potable water from a variety of wastewater (WW) sources including yogurt production (Davies et al. 1977), concentration of fruits and vegetable juices (Couto et al. 2011; Echavarría et al. 2012; Gunathilake et al. 2014) and pre-concentration of milk and whey (Balance et al. 2002).

Pilot-scale assessment of MBR-RO wastewater reuse revealed that the RO permeate quality in terms of conductivity, turbidity, organic content, ammonia, nitrate, hardness, E. coli, and the virus could meet the water quality requirements for many potable and non-potable reuse applications (Tam et al. 2007). However, the literature does not reveal much on the application of MBR-RO for fruit...
processing wastewater reuse. The present study would provide important information on membrane foulants, performance restoration and preservation techniques that support the community in the area for fruit WW reuse management.

Irrespective of the area of applications, the RO membrane will foul in time due to the layering of deposits. If these deposits are not promptly removed, the membrane’s permeation will be permanently disabled. Fouling is an extremely complex process that is related to site-specific variabilities, making it very difficult to generalize and analyze (Amy 2008). Feed water characteristics lead to foulant buildup, where contaminants in the feed attach to the membrane surface and block the permeation passage. Fouling is generally categorized into (1) inorganic fouling due to deposition of colloidal matters or inorganic scales on the membrane surface, and (2) organic and biofouling due to the attachment of organic substances coupled with microbial attachment and multiplication in the presence of adequate nutrient materials in feed water (Flemming 1997).

Proper process design, optimal pre-treatment of feed water, efficient operations and maintenance of process units and effective online management of membrane performance can prevent or reduce fouling to a great extent. At this stage, feed pre-treatment plays the most dominant role. If one is unable to remove all the fouling potentials from the feed water matrix, membrane fouling is inevitable with a sharp decline of flux along with permeate quality deterioration. As a solution, most membrane users go with chemical cleaning. Cleaning with chemicals for performance restoration (Ebrahim 1994) is a temporary solution that poses environmental concerns when discharging cleaning waste, with high operational cost. In addition, after several cleanings, membranes lose their permeation and rejection power, requiring replacement at a substantial cost.

In order to minimize chemical cleaning, online membrane performance management by physical methods is getting popular and does not involve chemical addition or plant shutdown. Use of well-pretreated feed and monitoring of the fouling initiation stages leads to preventive actions for steady performance. The rise of differential pressure across the membrane and the decline of the permeate flow suggest that online management is required. Online management includes forward flushing at higher flow/velocity of feed or backward flushing (UF, MF) and forward osmosis (RO). Forward osmosis works for processes that have high ionic concentration (conductivity) reject that stays side by side with the low concentration permeate head that is separated by a semipermeable membrane. Due to concentration differences, normal osmosis occurs, pulling water from the permeate side to the feed side, and cleans the pores of the membrane. As a new technology, the commercialization of forward osmosis is getting more discussions for critical water purifications (Yu et al. 2017).

The characterization of surface foulants is essential to decide the performance restoration strategy (online management, cleaning or pre-treatment). Guidance for flat sheet membrane operations, membrane surface and type of surface materials is easy to find. However, it is more challenging to find RO operations that use module configured membrane (spiral wound or hollow fiber). For RO studies, destructive autopsies of the module are needed, by cutting and opening the membrane. Foulant analyses are generally conducted by visual and microscopic examination of membrane surface deposits, chemical and biological analyses of foulants, as well as membrane surface scanning, microscopy and spectral evaluation of foulant materials (Jeong et al. 2015; Rahman et al. 2018). These procedures also support the characterization of the membrane.

Various foulant analysis techniques were applied in the present study. A parametric assessment was conducted on surface foulants from the surface of the RO membrane fed with actual MBR effluent (from a fruit processing plant) and treated effluent (treated actual MBR effluent with amorphous and solid surface sorption). Overview details on the treatment of the MBR effluent are given in Jamal-Uddin et al. (2019). The collected and analyzed foulant results were compared with that of a virgin RO membrane surface. In addition, foulants on the membrane were compared with flush-cleaned membranes. Membrane performance was restored by the online management of flush cleaning and use of preservation techniques. After initial operation with treated effluent, used membranes were preserved in air-tight containers. The solution pH was analyzed continuously to identify possible damage from low pH. Surface assessment was applied in all cases consisting of physical, chemical analysis and visual inspection of the membrane surface coupled with scanning electron microscopy (SEM), energy diffusive X-ray (EDX), Fourier transform infrared (FTIR) spectroscopy, Shimadzu TOC analyzer (calibrated, 99.5% validity) and contact angle measurements.

Currently, the study of RO membrane foulant analysis, performance restoration for industrial fruit processing wastewater undergoing tertiary treatment and preservation techniques has received minimal attention. The developed BMPs for RO membrane performance will assist processors in developing sustainable operations for the tertiary treatment of fruit processing wastewater.
MATERIALS AND METHODS

Developing BMPs requires various testing methods. This study investigated (i) operations of RO using synthetic effluent feed, (ii) RO operations feeding with actual MBR effluent, (iii) RO experiments using treated MBR effluent feed, (iv) membrane preservation and performance restoration (online management) and (v) foulant analyses on the surface of the membrane. An overview of the treatment of the MBR effluent is given in Jamal-Uddin et al. (2019). The focus of this study concerned the impact of the treatment of MBR effluent on foulants affecting the RO membranes. Comparisons were done with virgin and flush-cleaned RO membrane.

The MBR effluent for the study came from an industrial partner (IP) located in southern Ontario. Throughout the year, the IP washes mostly apples, but on occasion they treat other fruits. The wastewater system used by the IP consists of a membrane bioreactor (MBR) system, followed by a tertiary system consisting of a reverse osmosis (RO) and UV disinfection unit to polish the MBR effluent. Performance tracking shows that when the type of fruit was changed, fouling of the RO membrane increased, impacting the efficiency of the RO unit.

The influent wastewater was processed onsite by the IP. Briefly, it went through a biological treatment process (aerobic and anaerobic) followed by a 0.04 μm membrane (MBR) filtration of effluent water. Thus, no suspended organics or inorganics or colloidal particles (turbidity <0.1NTU) were detected in the effluent. The dissolved organics generated by the cell lysis of microbes during the MBR process in the form of EPS and soluble microbial products (SMP) were identified. Effluent characterization revealed the following ranges: BOD from 40 to 90 mg/L, COD from 60 to 110 mg/L, protein about 1–15 mg/L, humic substances from 40 to 70 mg/L and carbohydrates from 30 to 55 mg/L.

The organics present had very low molecular weight cut-off, which was consistent with the effluent passing through a 0.04 μm pore size membrane. These low-molecular weight SMP were inert and did not respond to any conventional pre-treatments including coagulation flocculation, media filtration, centrifugation, dissolved air floatation, electro-coagulation, or oxidation. Robust pre-treatments using eight coagulants and coagulant aids including poly-aluminum-chloride (PACL) and pre-treatment techniques as mentioned were evaluated. Finally, enhanced coagulation (EnC) based amorphous sorption followed by solid phase GAC sorption were successful in reducing SMP from 88.0 mg/L to about <2.0 mg/L, which were applied both for actual and synthetic effluent. It should be mentioned here that the gibbsite and amorphous solubility diagram was followed to catch the amorphous phase of Al (OH)₃ and Fe₂O₃ at about pH 6 and higher dosages of Alum (80–90 mg/L) and FeCl₃ (50–55 mg/L). Partial removal of SMP by amorphous sorption were conducted through settled amorphous. Complete details are reported in Jamal-Uddin et al. (2019) and Jamal-Uddin (2019).

Biofouling assessment and characterization of the membrane surface using the contact angle method was also conducted. The static contact angle (SCA) of the flat sheet membrane surface was measured by Dr Dipak Rana, of the Industrial Membrane Research Institute, University of Ottawa, Ottawa, ON, using a VCA Optima Surface Analysis System (AST Products, Inc., Billerica, MA). Prior to measuring SCA, the membrane was blotted using a piece of tissue paper and then dried at room temperature overnight. In the morning, a drop of liquid (1 μl of water) was placed on the flat sheet surface using a micro syringe (Hamilton Company, Reno, NV). The SCA value was recorded within a five-second period after a liquid drop was placed at five different spots on each flat sheet membrane sample. The SCA readings for the five values were then averaged. Analytical microscopy of the foulants on the membrane surface was conducted by (1) dissecting microscope, (2) compound light microscope, (3) scanning electron microscope (SEM) coupled with X-ray microanalysis for elemental analyses and (4) with a BRUKER FTIR spectrometer and associated infrared microscope. All those analyses were conducted at the Agriculture and Food Laboratory, Guelph (AFL 2018).

RO experimental setup

The RO system setup shown in Figure 1 was used for continuous operations using different effluents. The RO membrane tested in the experiments was the same one used by the IP, Filmtec polyamide thin film composite (PA-TFC) extra-low energy (XLE) RO membrane, Model BW30XLE (DOW, Midland, MI). Design flux for the system was 823–1023/8.6 LMH/bar), with a pore size MWCO of 100 Da. Polysulphone is the base material configuring the membrane. Operating pressure, as recommended by the membrane manufacturer, was maintained at about 125 psi at all times.

Synthetic effluent was used for some of the testing to provide consistency for testing. This also allowed collection of information on the impacts of individual contaminants.
towards membrane fouling and applicability of online management to restore RO membrane performance. Synthetic effluent was prepared by adding inorganic and organic ingredients to mimic the specifications of the actual MBR effluent. Different concentrations of SMP and extracellular polymeric substances (EPS) components, including inorganic chemicals, were added at varying concentrations to achieve the desired specifications (Table 1).

Bovine serum albumin (BSA) provided the protein component, with either humic acid or humic acid-sodium (Na) salt used to provide the humic substance content. One of the three saccharides D-lactose, dextrose and dextran were used as the hydrocarbon. The ranges of protein, humic substances and hydrocarbon contents in the actual effluent were measured, and were mainly determined by recommended methods and validated by TOC measurements for both synthetic and actual MBR effluents.

Parametric investigation and development of various pre-treatment techniques – enhanced coagulation and selection of efficient high rated granular activated carbon sorption, as outlined in Jamal-Uddin et al. (2019), were applied to treat the synthetic and actual MBR effluent. In summary, enhanced coagulation coupled with liquid phase amorphous and solid-phase GAC sorption provided a treated feed from the actual MBR effluent that achieved the desired quality (NTU < 0.3, TOC < 5) for RO operations.
RO operations

Foulant analyses were conducted for membranes operated with actual MBR effluent and treated effluent. Surface analyses were also conducted for the flush-cleaned membrane and the virgin membrane to compare the impacts of treatment and flush-cleaning with the virgin membrane. Feedwater turbidity was maintained to <0.3 NTU except for the synthetic effluents. For the synthetic effluent runs, only the surface of the membranes was physically inspected and photographed. No FTIR or SEM analysis was conducted, as this was not considered part of the main-stream RO feed.

The RO operating feed pressure for all the cases was 125 psi as prescribed by the membrane manufacturer. The feed flow was about 2.54 LPM (0.67 GPM). The membrane was fed without any up-stream pre-cartridge filtration (10 μ), which is normally used at the suction of RO HPP (high-pressure pump) at the real plant site. Both permeate and reject were returned to the feed tank for circulation operation. Prior to recirculation to the feed tank, reject temperature was controlled (reduced) to adjust with feed temperature. After a couple of hours, as required, the actual MBR effluent feed in the feed tank was changed with a fresh one. The RO operations were continued uninterrupted until the desired hours of operation were achieved.

Feed and permeate flow, conductivity, along with reject flow and temperature, were measured continuously. Permeate flow was normalized to 25 °C for all batches of operations using temperature normalization factors collected from the membrane supplier.

Membrane preservation was conducted in DI (deionized) water in an air-tight container to avoid contact with air and air oxidation. The preservative pH was measured regularly and maintained between 4.5 and 7 to save the membrane from acidic/oxydation damage. After every two weeks, the DI preservative was replaced with a fresh one. After 3 to 4 months of preservation, the used membrane was operated to verify its performance post restoration.

Foulant analyses

Foulants were scraped off the membrane surface and dried prior to inorganic analyses. The analyses consisted of visual, physical and chemical as well as microscopy and EDX. The respective membrane samples were cut and dried for the SAM EDX assessment. The residues scraped from the membrane surfaces were smeared onto a sample slide containing KCl solution. Following preparation, the slides were analyzed using a FTIR spectrometer and an associated infrared microscope to identify organic structure and functional of foulants. The spectra were compared with known compounds in the databases to get a match or closest match to a known structure.

Bacterial enumeration was conducted following the procedures recommended by Farooque et al. (1997). Aseptically, pieces of membranes were obtained and soaked in sterile effluent. The foulant attached to the membrane piece was scraped out aseptically and transferred to a test tube and mixed on a vortex mixer. Serial 10-fold dilutions were carried out to determine the number of bacteria per unit area of membrane. Pour plate counts were prepared using A3340 All Culture (AC) Agar (Sigma Aldrich, Oakville, ON) for microbiology. AC Agar provides for an early and luxurious growth of a diverse group of aerobic, anaerobic and microaerophilic microorganisms. The total microbial count was determined 48 h after incubation at 35 °C.

Online management and performance restoration

The IP reported that the online management of membranes was not successful, so performance restoration via chemical cleaning of the RO membranes was investigated. The process mimicked what the IP was doing, a weekly cleaning consisting of 1-hour circulation at high pH (12) adding NaOH for clean-up of organic foulants followed by subsequent 1-hour recirculation with fresh water at pH 7 to bring the system back to the neutral pH range. In the third hour, cleaning at low pH (3-4 by adding HCl) was conducted by recirculation to remove inorganic foulants. To bring the pH at the neutral range, the fourth-hour circulation was maintained at pH 7.

In spite of incurring all those chemical and operational costs, performance restoration could not be achieved, and flux decline continued. Consequently, non-chemical online management was tested in the laboratory using the flush-clean technique. The RO membrane was operated for 5 to 10 minutes at low pressure with a flow rate that was 3 to 4 times higher to wash away the loosely bound deposits from the surface of the membrane, as well as back flow (osmosis) of permeate through the membrane pores to remove the foulant inside the membrane.

RESULTS AND DISCUSSION

Experiments were completed on the ability of a RO unit to treat synthetic and actual MBR effluent and treated MBR effluent. Additional investigation centred on membrane
surface foulant analysis, online performance management, membrane performance restoration and used membrane preservation. Characterization of a fouled membrane, including comparison with virgin membrane surface, was also conducted.

RO operation with synthetic effluent

Operations with untreated synthetic effluent revealed that the membrane flux declined very sharply, with about 58% of the initial flux decline from 2.69 mL/min (36.6 LMH) to 1.15 mL/min (15.8 LMH) happening within 40 hours of operations. For simplicity and easy understanding of flux (LMH – L/m²/h) is reported as (mL/min) in all subsequent figures. Figure 2 shows the RO performance in terms of permeate flow vs operation in hours for treated and untreated synthetic effluent. The overall behaviour was similar for both effluents, showing that the synthetic effluent was not reasonably treated for fouling organic protein.

Coagulation-sedimentation was applied by adding different coagulant dosages at the maintained optimum pH of 6.0–6.3, following the process identified by Jamal-Uddin et al. (2019). The optimum pre-treatment of synthetic effluent consisted of adding coagulant alum (80 mg/L) along with chitosan (38 mg/L) as the aid. These amounts improved effluent quality by coagulating suspended particles in synthetic effluent, reducing conductivity from 2,200 μs/cm to about 431 μs/cm with coagulating ionic inorganic salts. Turbidity decreased from 10 to 0.50 NTU, but no improvement in flux decline was observed, as seen in Figure 2. This is reasonable due to the artificial protein (BSA) in the synthetic effluent that was not removed.

The synthetic effluent contained TSS, color (10 Pt-Co) colloidal materials (NTU 10), macromolecular SMP and EPS components (protein, carbohydrate, and humic substances). Most of the compounds in the synthetic effluent dropped significantly in value, with the exception of protein, which caused the RO flux to decline in the case of RO operations. This suggests that the macromolecular SMP components, specifically Bovine Serum Albumin (BSA) were not sorbed by the liquid amorphous phase or the solid-phase GAC surface. However, Jamal-Uddin et al. (2019) observed that the micromolecular EPS that had a size less than 0.04 μ, the MBR pore size, were sorbed by the GAC treatment.

The adverse impact of protein was also noticed, where protein increased the turbidity and was difficult to reduce using enhanced coagulation. The observed RO flux decline due to protein can be attributed to the lower effectiveness of turbidity reduction in pre-treatment, which caused RO fouling. However, humic substances were removed by both the enhanced coagulation and the RO filtration, as noted by Agui et al. (1992), and are less involved in the flux decline.

RO operations with actual MBR effluent

A series of RO experiments was conducted with actual MBR effluent. Figure 3 shows the gradual flux decline that was observed, indicating that the RO membranes were getting fouled.

The upper curve in Figure 3 (first effluent) had a TOC of 88 mg/L, and allowed for slightly higher permeation when compared to the lower curve (second effluent) having a TOC of about 275 mg/L. Other parameters including color, COD, and TDS were also higher in the second effluent to about 21 Pt-Co (color), 550 mg/L (COD) and 682 mg/L (TDS). All contributed to lowering the permeation from the second effluent. Both flux decline rates were different, with the flux from the first effluent reduced to about 64% in 110 hours of operation, while the second effluent reduced to about 50% in only 69 hours of operation. Thus, it may be concluded that flux decline was dependent on actual DOM
concentration in the MBR effluent. The higher the DOM content, the quicker/steeper the flux decline.

The IP had implemented a chemical cleaning process to reverse the observed flux decline. Despite the four-stage process involving NaOH, which incurred chemical and operational costs, performance restoration could not be achieved, and flux decline continued. A small study was undertaken using other chemical agents including citric acid (1% wt.), detergent (0.5% wt.), at pH 11 by adding NaOH), sodium bisulphite (SBS, 0.5% wt.) and sodium hexametaphosphate (SHMP, 1% wt.) based on the previous work of Farooque et al. (1997). Restoration was not very successful. This is the challenge with cleaning protocols, which can be compounded by manufacturers who suggest the use of proprietary cleaning agents. Any kind of chemical cleaning has both economic and environmental burden without any assurance of restoration. In addition, there is membrane deterioration. As such, non-chemical online performance management using high flow flushing along with preservation and performance restoration of the used membrane was considered.

The online flushing consisted of the following sequence. After 80 hours of operations, the first membrane was flushed for 5 minutes at a higher flow (3.4 LPM) low-pressure feed to disrupt the foulant and restore membrane performance. A small increase in flux rate was observed for a short period of time. In a similar operation, by increasing the flushing velocity from 85 to 225 cm/s as suggested by Braghetta et al. (1998), significantly positive results were reported. The flux decline rate was higher with synthetic effluent compared to actual MBR effluent, most probably due to the presence of macromolecular organic compounds of SMP and EPS in the synthetic effluent. The SMP and EPS compounds caused about >70% flux decline in less than 70 hours in some cases. Higher flux decline at high initial flow and pressure was a general trend, where high-pressure compaction and cake layer scaling was the cause of the decline in the Braghetta study. This was not the case in the present study, showing that the IP could adopt the suggested online flushing BMP to maintain a high flux rate.

Calcium and magnesium are also fouling culprits (Tang et al. 2007), but fouling by calcium and magnesium were not observed in this study.

**RO operation with treated effluent**

Utilizing the enhanced coagulation and GAC treatment strategy outlined in Jamul-Uddin et al. (2019), the treated MBR effluent had a TOC of about 2 mg/L and turbidity of about 0.28 NTU. Both these values were well below the recommended characteristics of RO feed (TOC < 5 mg/L and turbidity < 0.3 NTU). RO operations with the treated effluent showed steady performance in terms of permeate flux/flow vs hours of operation. However, there was a slight decline in flux after about 90 h of continuous operation. Low pressure and high flow feed flushing for 5–10 minutes restored the declined flux to its original value. This could be attributed to the loosely bound water mould or suspended amorphous particles, but not Ca, Mg or other microbial.

Flushing results suggested that intermittent program flushing can be implemented to maintain steady membrane performance. Surface deposits that were loosely attached could easily be removed by hydrodynamic disruption of the deposit materials without using any chemicals, leading to successful on-line membrane performance management and restoration. Avoiding the use of chemicals saves the environment from cleaning waste disposal along with the benefits of reduced operational costs. Treated effluent conductivity was not a concern as it was very low (400–500 μS/cm) in all cases. The RO permeate conductivity was reduced to 10–15 μS/cm after RO filtration, resulting in about 98% rejection.

**RO membrane preservation**

RO membrane plants (or any other process plants) require breaks or shutdowns, most often for different reasons including maintenance, foulant cleaning, membrane changeover, feedwater quality rectification, and annual shut down for overhauling. For most of the cases, membranes are left in the stand-by mode in the system, without taking any precautionary measures to protect the membrane in shutdown conditions. However, in this condition, immediately after shutdown, there exist foulant materials on the surface of the membrane, and the membrane remains flooded with brine that contains a high concentration of foulants. In the presence of the foulant materials, biofouling starts and blocks the membrane pores by forming a permanently fixed layer on the surface (Al-Mobayed et al. 2005). Overtime, the membrane physical properties deteriorate and ultimately lose their permeation power. As a preventive measure, the membrane should be preserved in a suitable solution.

Immediately after shutdown, membranes should be flushed with a preservative solution and left flooded with the solution, keeping the membrane wet without material damage from dryness. Hassan et al. (1997) tried three biocides as preservation chemicals for seawater reverse...
osmosis (SWRO) membrane but found that simple SWRO permeates or DI (deionized) water at the neutral pH could be a suitable membrane storage solution. As such, a similar procedure was applied in the present study for fruit wastewater using only DI water.

Several RO membranes after treating effluent for about 100 hours were preserved in DI water in an air-tight container. The pH of the preservative was monitored continuously to maintain the pH in the neutral range. The DI water was changed twice a month. After about four months of preservation, the membranes were again used to process treated MBR effluent. Figure 4 shows that membrane performance remained unchanged after 4 months of preservation. As such, combining proper storage with the suggested BMP for online flushing, gives the IP a good restoration technique for steady membrane performance, maintaining maximum performance of the RO unit.

**Foulant analysis**

In all applications, the RO system gets deposits on the membrane in course of operations. Depending on the characteristics of the deposit, the membrane can be fouled either reversible or irreversible, plus any physical impairments that may happen. Characterization of the deposits on the membrane surface is essential when planning a strategy to decide on the types of precautions or pre-treatments needed.

Visual inspection of all the membranes operated in this study showed that no physical damages occurred. Thick reddish-brown deposits were observed that were denser in the case of synthetic effluent when compared to the actual MBR effluent, indicating that the membranes were fouled from the untreated feed. However, unlike biofilms, which are very sticky to the surface of the membrane, the observed deposits could be easily scraped off the surface. In the case of synthetic effluent, foulants were known from chemical addition to make up the effluent, so further analyses were skipped.

**Foulants on actual MBR effluent operated membranes**

The physical appearance of collected foulant was amber in color and appeared to be sheets of amorphous materials with some inclusions. The presence of some carbonate materials was presumed as a mild bubbling reaction occurred when treated with concentrated hydrochloric acid. No plant materials were noticed in the foulants.

Foulant material analyses using SEM with an X-ray micro-analysis system revealed elements of oxygen (O), iron (Fe), zinc (Zn) silicon (Si), aluminum (Al) and sodium (Na) along with smaller proportions of calcium (Ca), magnesium (Mg), phosphorous (P), sulphur (S), potassium (K) and copper (Cu) as shown in Figure 5. The majority of these elements could be attributed to a corrosion by-product from system components of galvanized (Zn-plated) iron/steel materials. Visually observed corrosions of vessels and piping at the plant supported the assumption. However, the high pick of oxygen, associated hydrogen, and carbon revealed the alcholic, acidic and amine functionality of organic compounds, which were both from the foulants and membrane materials.

Foulants analyses using a FTIR spectrometer and associated infrared (IR) microscopy spectra showed functional groups of foulants over the membrane surface. The peaks in Figure 6 do not represent a single compound, but rather a mixture of compounds. The peaks at wavenumbers of 1,040 and 2,940 cm$^{-1}$ indicated the presence of polysaccharide-like materials. A very broad peak in the region between 3,100 and 3,600 cm$^{-1}$ indicated the presence of exchangeable protons, typically from alcohol, amine, amide, or carboxylic acid having -OH, -NH2, -CONH-, or -COOH functionality, respectively (Marlic et al. 2003). Peaks at 1,550 and 1,640 cm$^{-1}$ were pieces of evidence of the presence of protein-like materials (Jarusutthirak & Amy 2006), which reasonably correspond to the building block of bacterial cell walls and are transmitted to SMP through the cell-lysis process. Foulants were concluded as polysaccharides and amino sugars (building block of protein) major. Zhu et al. (2011) found protein-like substances, polysaccharides, and SMP like materials by FTIR analyses from fouled RO membrane, fed with wastewater MBR effluent. Observations with FTIR analyses are in agreement with the DOC (80–90 mg/L) and EPS measurements in the actual MBR effluent water. The amber color indicated the presence of humic substances.

**Foulants on treated effluent operated membranes**

Visually, there appeared to be a very small amount of foulants on the RO membrane surface when operated with
Figure 5  | (a): ED X-ray spectrum of foulants collected from RO surface operated with actual effluent. (b): ED X-ray spectrum of foulants collected from RO surface operated with treated effluent.

Figure 6  | FTIR spectrum from foulants on RO surface fed with untreated MBR effluent.
treated MBR effluent. Compared to foulants observed on the surface of the RO membrane when using untreated MBR effluent, the observed foulants were remarkably reduced. However, the material was very hard to remove and appeared to be largely just pale yellow-orange color staining on the surface, translucent with amber to yellow shines. The yellow staining was observed on the top layer of the sulfone base membrane, possibly from iron and zinc salts. However, no metal particles/dust were noticed. So the colour source is not clear at this stage.

The material was scraped from the membrane surface and assessed using SEM-EDX and was composed primarily of Al, Fe, S, C, O, Zn, Si, P and a trace amount of Ca. The observed Fe and Al was an obvious part of the coagulants added for treatment and maybe in the form of alumina (Al₂O₃) and iron oxide (Fe₂O₃), which escaped from precipitation during coagulation. These amorphous metals along with natural particles probably contributed in deposition. In comparison to untreated MBR effluent, there was a significant reduction of Si (from 1,500 to 400 counts), Ca (from 400 to 100 counts), and O (from 4,200 to 1,000 counts). The reduction of O and H were indicative of lower organic concentrations. A consequence of the reduced values is a reduction in irreversible foulants when compared to untreated MBR effluent. Calcium and Si are the two members that generally promote hard scaling, and both were reduced substantially, see Figure 5(b).

FTIR analysis showed that the functional curves have the closest match with poly-sulfone polymer, as shown in Figure 7. Poly-sulfone is part of the membrane materials, a base on which the polyamide polymer was cast during membrane manufacturing and is represented by the lower curve in Figure 7. Compared to the lower curve, the upper curve appears to be almost a match with the membrane base material, poly-sulfone, indicating that there is no foulant on the surface of the flush-clean membrane. In the absence of organic foulants that were removed during the coagulation pre-treatment stage, loosely bound metallic depositions were easily removed during a flushing operation.

Post flushing, there is a good match of the flush-clean membrane (upper) with that of the poly-sulfone membrane base. This can be seen by comparing Figures 6 and 7. Figure 6 has peaks at wavenumbers of 1,040 and 2,940 cm⁻¹ (polysaccharide), at 3,100 and 3,600 cm⁻¹ (alcohol, amine, amide, or -COOH), and at 1,550 and 1,640 cm⁻¹ (protein), which are not seen in Figure 7. The absence of these noted peaks shows their removal by the coagulation and flush-clean operations.

It should be noted that no CF (cartridge filter) was used ahead of the RO membrane at bench-scale experiments. However, in the actual plant, there would be a mandatory 10μ cartridge filter (CF) ahead of the RO high-pressure pump. It is expected that the CF should take care of those loose depositions. As a result, flushed cleaning can be significantly reduced in the real plants.

Figure 7 | FTIR spectrum from foulant on RO surface flushed at low pH after operation feeding with treated water (upper curve), the foulant has the closest match with polysulfone (lower one).
Foulants on flush-cleaned membranes

Following high flowrate flushing, the RO membrane surface became very clear. Scraped materials from the membrane surface were very clear to powdery white, which could be attributed to the amorphous alum products (turn to white powder after drying). There appeared to be no collectible material or residue on the surface of the membrane. The material scraped from the surface of the flushed membrane was analyzed using SEM-EDX, showing the majority of Al, Si, C and O present, with traces of P, Fe, Ca and Zn having no significant fouling impacts. Al and Si are from coagulants and C and O are elements of membrane materials.

Figure 8 is the FTIR analysis of the surface materials. The closest match of these materials on FTIR spectral analyses was found with an amine-based activator in the system database. The curve seen in Figure 8 most presumably resulted from the poly-sulfone and polyamide mix (membrane materials) that were collected from the membrane surface by deep scraping. The membrane used in this study was made of poly-sulfone base polyamide. Although traces of an amine/amide (membrane material) along with aluminum salts were assumed, no metal particles or dust were noticed in the surface material. Very low dissolved organic carbon (2 mg/L) was present in the treated feed, which does not support any effluent-originated organic fouling. At a very low (about <10%) recovery from a flat sheet membrane, there is no possibility of increased DOC concentration polarization exceeding the proposed threshold limit of 5 ppm on the surface of the membrane. It could hardly reach up to 2.2 mg/L, which generally will not support fouling. Organic peaks were attributed to membrane materials only.

Virgin membrane surface examination

The top layer of a virgin RO membrane was also analyzed for comparison of SEM-EDX and FTIR results with those foulants from treated effluent and flushed-cleaned membrane surfaces. The SEM-EDX analysis of virgin membrane showed S, C, and O with a trace of Si and Cl, which were elements from membrane materials, poly-sulfone based polyamide. Poly-sulfone is a sulfur-based polymer represented by a high peak of S, while C and O are elements of organics of membrane materials. Figure 9 shows a comparative assessment of the three FTIRs: the virgin, treated effluent operated and flush-cleaned membranes. The upper curve (a) is from the RO membrane surface material while operated with treated effluent, the middle red curve (b) is from the materials from the surface of the membrane after high flow flushing during treated effluent operation, and (c) the lower one is from new (virgin) RO membrane surface material. Comparing the three curves reveals that curves from the flush-clean and new membrane are almost similar (good match), indicating that no foulants were present after the flush-clean. The upper curve (a) has a remarkable peak at 1,040 cm$^{-1}$ indicating the presence of polysaccharide in treated water. However, there are no remarkable peaks at 3,100 and 1,640 cm$^{-1}$, showing no protein and other CH materials in the foulants.

Bio-fouling evaluation

The positive results of the flush-cleaning suggested that foulants on the membrane surface from the treated effluent operated membrane were loosely attached. After being
flush-cleaned, the membrane performance returned back to its original position. Biofouling is a bio-film problem (Flemming 1997), which is sticky to the surface and not so easily removable. Usually, the bio-fouled membrane, on which the biofilm forms, tends to contain above 70% of organic matter (Flemming 1997). FTIR analyses did not show any extra organic matter on the membrane surface other than membrane materials. Furthermore, while treated effluent was stored for about 5 months, no change in initial TOC (2 mg/L) was observed, suggesting that it contained limited biodegradable organic matters (BOM). Accordingly, the possibility of biofouling was ignored and for this reason did not propagate the biofouling process on the membrane surface. On the other hand, the latest collection of actual MBR effluent revealed the presence of additional BOM as the initial TOC increased from 200 mg/L to 360 mg/L in 3 weeks storage time. This suggests that the actual MBR effluent had high biofouling potential, unlike the treated effluent, where almost all the BOM was removed during treatment.

Membrane characterization by contact angle

Generally, contact angle in the range of 0°–90° identifies a surface to be hydrophilic (water-liking), and that of an angle of 90°–180° is for a hydrophobic (water-disliking) surface. However, for membranes the line of demarcation between hydrophobicity and hydrophilicity is reported to be a 50° contact angle for water on the membrane surface (Childress & Brandt 2000). With this demarcation, membranes with a contact angle slightly above 50° are slightly hydrophobic, while those slightly below 50° are slightly hydrophilic in nature. The present results contradict the Childress and Brandt findings as the measured contact angle range for virgin membrane was (47°–79°). However, findings on the heavily fouled membrane when operated with the actual MBR effluent provided similar results to that of Childress & Brandt (2000).

For the actual MBR effluent, the RO membrane surface the contact angle (CA) was 28°, while the flushed-cleaned RO membrane had a contact angle of 76°–79°. These contact angles show a contradiction with the provided CA definition and were probably due to the highly fouled membrane, with a heavy-layered cover by the organic and inorganic foulant. This meant that the water molecules could not make contact with the RO membrane surface. A similar observation was also reported by Childress & Brandt (2000) from a highly fouled membrane. It can be concluded that a very high-thickness layer of foulant on the membrane surface minimizes contact of the water drop with the membrane, so the measured value is irrespective of the membrane surface.

Present results with the treated MBR effluent reveal that the contact angle was substantially changed after the RO membrane got fouled. However, when the surface was flush cleaned during online management, the contact angle value returned back to the original virgin membrane, which suggests that the online management was successful in cleaning the RO membrane surface. The contact angle results reported here agree well with other studies (Decker et al. 1999; USBR 2000) on the behaviour of a hydrophilic membrane.

CONCLUSIONS

Best management practices (BMPs) were successfully developed for post-treatment of MBR effluent to allow sustainable
permeation and performance of a tertiary RO system. Results from RO operations using treated and untreated MBR effluents revealed that steady RO performance was challenged by foulant deposits on the membrane surface. These deposits could easily be removed by a combination of enhanced coagulation and GAC sorption treatment of the MBR effluent to reduce the DOM levels, producing a foulant-free feed. There was no sign of bio-fouling or organic deposits. Once the MBR effluent was treated, any decline in the flux of RO can be restored by applying online flushing for 5 to 10 min at a higher flowrate to remove loosely bound deposits on the membrane surface. Studies also showed that in offline conditions, the used membrane should be preserved in a deionized water at neutral pH to keep the membrane fresh, providing constant permeate flow without any deterioration once back in operation. The IP and other processors in the sector will benefit from the developed BMPs to maintain sustainable management of fruit wastewater by minimizing fouling and subsequent cleaning problems.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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