Reverse osmosis fouling during pilot-scale municipal water reuse: Evidence for aluminum coagulant carryover

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ABSTRACT

Surfaces of two reverse osmosis (RO) membranes, one from each stage of a real-world pilot-plant operated in support of full-scale design of municipal water reuse, were extensively characterized to determine dominant foulants. Since the source wastewater was purified using extended aeration activated sludge, alum was also being added to the secondary clarifier to eliminate potential problems with colloidal sedimentation. Even though microfiltration (MF) was implemented to pretreat the secondary effluent prior to RO, significant aluminum fouling was detected by energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Peak shifts in Fourier transform infrared (FTIR) spectra and high resolution X-ray spectra indicated aluminum complexation with the membrane surface. Calcium and phosphorous (from added antiscalant) were also detected along with only weak signals from organic matter suggesting the dominance of inorganic fouling. These results demonstrate that chemicals added during wastewater reclamation can foul downstream membranes necessitating careful monitoring of existing wastewater treatment unit operations and RO pretreatment processes. One-step cleaning with EDTA at pH 11 successfully removed both aluminum and calcium and restored the flux to nearly that of the virgin membrane. In contrast, citric acid at pH 4 was effective in removing calcium but not aluminum and did not fully recover the flux. Hence, flux decline appears to be closely linked to aluminum rather than calcium deposition. Residues of EDTA and citric acid were detected on the cleaned membrane surface even following multiple rinse/washing cycles. Although this did not impact short-term flux recovery, the effects of such remnants on long-term membrane life and flux restoration following multiple cleaning cycles need further investigation.

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1. Introduction

Factors such as population growth, climate change, and drought have reduced the availability of high quality water sources sometimes necessitating wastewater reclamation to meet our growing demands for drinking water. Purifying municipal wastewater to drinking water standards requires a series of advanced technologies serving as multiple, redundant barriers against myriad contaminants (i.e. the multiple-barrier approach) [1]. Reverse osmosis (RO) is almost universally employed during water reuse as the final filtration step to remove numerous trace organic compounds including contaminants of emerging concern, disinfection by-products and their precursors, etc. [2,3]. However, like in all other RO applications, colloids, organic matter, precipitated salts, and microorganisms tend to accumulate on, in, or near the

membrane surface reducing the overall water permeability; i.e. cause fouling [4,5].

To reclaim/reuse wastewater effluent, our current practice is often to simply append all necessary advanced technologies, including RO to existing unit processes without any changes to the treatment plant. However, much of our current civil engineering infrastructure is ageing and outdated [6]. Hence, even if the secondary-treated effluent meets all regulatory permits (mainly biochemical oxygen demand and total suspended solids), it could still contain substantial amounts of non-biodegradable organics, inorganics, and submicron colloids, since they aren't covered by federal or state water quality standards. Hence, to reduce the migration of these possible foulants to the RO system, existing wastewater treatment unit operations need to be tightly controlled and possibly even upgraded for the successful operation of the retrofitted water reuse treatment train. However, this issue is often not considered during the design and implementation of advanced water reclamation technologies.

RO fouling during water reuse is commonly reduced by treating the secondary effluent using microfiltration (MF) or ultrafiltration

(UF) [1,7–10]. However, MF/UF only remove colloidal foulants such as turbidity, bacteria, and high molecular weight organic matter and therefore only partially control RO fouling [8,11]. Additional MF/UF/RO fouling control can be achieved by dosing coagulants to enhance the removal of colloidal, dissolved, and macromolecular foulants [12,13]. In some cases, coagulation may already be employed to enhance liquid-solid separation in the secondary clarifier [14], capable of enhancing the flux of any downstream membranes employed for water reclamation [15]. However, as described above, the coagulation conditions may not be properly controlled resulting in overdosing, since aluminum or iron are not included in effluent permits. But, improper coagulant control can exacerbate fouling, which has been demonstrated during surface water treatment and desalination [12,16,17] but not for water reclamation.

Foulants can be identified by sacrificing the RO module and examining the membrane surface spectroscopically and microscopically at the conclusion of testing, i.e. performing an "autopsy" [18]. Autopsies have revealed that organics of microbial origin (i.e. proteins and polysaccharides), humic-like compounds, as well as calcium, sulfur, silicon, and phosphorous are major RO foulants during wastewater reclamation [3–5,7,19]. Also, bioorganic fouling typically dominates lead elements while inorganic fouling contributes more for tail elements [5]. Autopsies on RO membranes following conventional (i.e. coagulation, flocculation, sedimentation, and media filtration) pretreatment during brackish water desalination have shown that any residual coagulant can also cause fouling [16,17,20]. These investigations focused more on bulk water chemistry and operational data to infer that aluminosilicates and aluminum hydroxides were possible foulants. Detailed surface characterization and specific coagulant-membrane interactions were not pursued.

The primary objective of this research is to perform autopsy of RO membranes used to reclaim wastewater which underwent secondary treatment including alum coagulation to determine relative contributions of organic and inorganic fouling. Fouled RO elements obtained from a pilot-scale study conducted in support of full-scale plant design were extensively characterized using Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometry (SEM-EDS), Fourier transform infrared (FTIR) spectroscopy, and X-ray Photoelectron Spectroscopy (XPS) to determine dominant foulants present on membrane surfaces. Based on autopsy results, citric acid at pH 4 and EDTA at pH 11 were selected as simple 1-step cleaning agents. Their regeneration efficacy was assessed by measuring the hydraulic permeability and characterizing the surfaces of cleaned RO membranes.

2. Experimental work

2.1. RO pilot-plant and pretreatment

The municipal wastewater was treated at full-scale with an extended aeration activated sludge process followed by tertiary treatment using single-stage media filtration, ultraviolet disinfection, and post-aeration. Alum (aluminum sulfate) was added to promote colloid coagulation and sedimentation in the secondary clarifier. The pilot-plant was designed to evaluate the possibility of reclaiming only the secondary effluent water (i.e. after aeration, alum addition, and secondary clarification) by MF and RO as shown in Fig. 1. In other words, tertiary treatment unit processes were not included for RO pretreatment and wastewater reclamation. A 2 mg/L chloramine residual was maintained in the MF feed water by pre-ammoniation to control biofouling. Over the duration of the study, the average total organic carbon concentration, 5-day biochemical oxygen demand (BOD_5), and chemical oxygen

demand (COD) of the RO feed water were 6.3 ± 0.5 mg/L, < 2 mg/L, and 22.3 ± 4 mg/L, respectively. Note that alum also successfully removed phosphorus, which was below detection limits in the microfiltered wastewater. The alkalinity (buffering capacity), total dissolved solids, calcium, sodium, chloride, and sulfate concentrations were 106.8 ± 14.3 mg/L as $CaCO_3$, 1117.1 ± 35.5 mg/L, 110.0 ± 8.2 mg/L, 222.9 ± 11.1 mg/L, 298.6 ± 10.7 mg/L, and 143.3 ± 23.2, respectively. A proprietary phosphonate-based *anti*scalant was added before RO. The two-stage RO system was operated at an overall flux of 19 L/m^2-h and 85% recovery with concentrate recirculation in the second stage.

2.2. RO membranes

Two fouled 4-inch diameter thin-film composite spiral wound RO elements (KOCH HR-4040), one from each stage of the pilot plant, were brought back to our labs for further analysis. Coupons of the virgin membrane were also purchased from the manufacturer to serve as controls, the contact angle of which was measured to be $35° \pm 1.8°$ similar to previous reports [21,22] demonstrating its hydrophilic nature. Upon receipt both membrane modules were visually inspected revealing that the fiberglass casings, permeate tubes, and brine seals were all in a good condition showing no signs of physical damage or external contamination. The module was sacrificed and central portion of the membranes were cut into flat sheets, stored in moist sealed plastic bags, and preserved at 4 °C in a refrigerator before further analysis. A minimum of three coupons from different locations on the membrane element were characterized by SEM-EDS, XPS, and FTIR.

2.3. Scanning electron microscopy and elemental analysis (SEM-EDS)

Prior to analysis, membrane coupons were further cut into smaller pieces and dried in a vacuum desiccator for 24 h. A scanning electron microscope equipped with X-ray microanalysis (SEM-EDS) was also used to obtain preliminary information on the overall surface elemental composition of the virgin and fouled membranes. These measurements were made using a JEOL JSM-6010LA InTouchScope SEM with integrated Energy Dispersive X-ray Spectroscopy (EDS) analyzer at an acceleration voltage of 15 kV, 10 mm working distance, and $250 \times$ magnification.

2.4. X-ray photoelectron spectroscopy (XPS)

More detailed information on the surface elemental composition of virgin and fouled membranes were obtained with a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.7$ eV) incident at 90° relative to the axis of a hemispherical energy analyzer. The neutralizer was turned on to reduce charging of the non-conductive polymeric membranes. Survey spectra were obtained over the entire range (0–1400 eV) and high-resolution spectra were obtained for photoelectrons emitted from C 1s, O 1s, and Al 2p regions to verify surface functionalities. Prior to high resolution scans analysis, the electron binding energy was calibrated initially with respect to the adventitious C 1s line at 284.8 eV. Component peaks were deconvoluted using the Shirley routine assuming mixed Gaussian-Lorentzian shapes and correcting for sensitivity factors after integrated baseline background subtraction. Using this procedure, the C 1s peak was resolved into four components: (1) aromatic or aliphatic $\underline{C}$-(C,H) at 284.8 eV, (2) a peak at 286.0 eV attributed to $\underline{C}$-(O,N,OH), (3) a peak at 287.8 eV from C=O, or N–C=O, and (4) a weak peak at 288.9 eV arising from O=$\underline{C}$-OH and O=$\underline{C}$-OR. Similarly, O 1s region was decomposed to: (1) a peak at