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Extremely fouling resistant zwitterionic copolymer membranes with ~ 1 nm pore size for treating municipal, oily and textile wastewater streams

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ABSTRACT

In this study, we document the performance of novel zwitterionic copolymer membranes with a molecular weight cut-off (MWCO) of around 1 kDa in treating municipal and industrial wastewater streams. These membranes were prepared by forming selective layers of self-assembling zwitterionic amphiphilic random copolymers on porous supports by a simple coating method. In single- and mixed-solute fouling tests with common components of effluent organic matter in municipal wastewater feeds (polysaccharides, natural organic matter, and fatty acids), these membranes showed complete resistance to irreversible fouling. The same excellent fouling resistance was also observed with oil emulsions common in industrial wastewater. One membrane showed no decline in flux even during the 7-day dead-end filtration of an oil emulsion, which is an unprecedented degree of fouling resistance. Both membranes also exhibited no irreversible flux decline after filtering real wastewater samples from a textile dyeing plant in Turkey. High rejections of dyes and colored substances were achieved, while salts were allowed to permeate. This allows for low pressure operation. The effluent can potentially be reused with minimal post-treatment. Thus, zwitterionic copolymer membranes are very promising for municipal and industrial wastewater treatment and reuse.

1. Introduction

Reclamation and reuse of wastewater is crucial for the protection and sustainable utilization of water resources. Wastewater streams contain complex mixtures of pollutants such as organics, solids, inorganics, emulsions, toxins and pharmaceuticals [1]. The complexity and variability of their composition makes adequate treatment for environmental discharge and reuse challenging, as does the high concentrations of pollutants [1,2]. Membranes are a core technology for water and wastewater treatment that offers modularity, small footprint, and better effluent quality compared with conventional technologies [3,4]. Ultrafiltration (UF) membranes are designed to remove microbial and macromolecular contaminants and oil droplets with low salt retention, and typically feature 2–100 nm pores, characterized by their molecular weight cut-off (MWCO). UF membranes are used in municipal wastewater reclamation [3] for treating primary or secondary wastewater effluents [5–8] or to pretreat water before nanofiltration (NF) or reverse osmosis (RO) to remove salts [9] or organic chemicals [10]. Depending on feed composition and the MWCO of the membrane, UF membranes may or may not sufficiently reject organic pollutants for reuse or fouling prevention [11–14].

UF membranes are also extensively used in industrial wastewater treatment and reuse in textile [15], petroleum refining [16] and other chemical industries. The presence of foulants such as oil and different needs for effluent quality for disposal or reuse present additional challenges to treating industrial wastewater. Oily wastewaters are generated from food, textile, oil and gas, petrochemical processing, and metal finishing industries [16–18]. A membrane that can effectively remove emulsified oils and resist fouling by oily and fatty acid components would be very promising for these applications.

Wastewaters from the textile industry originate from various pretreatment, dyeing, printing, and finishing steps [19–25]. These streams contain synthetic dyes, salts, oil droplets and additives such as surfactants, complexing agents, and fatty residues. Most UF membranes cannot effectively remove dyes due to their small molecular size and their chemical diversity [26]. NF membranes provide better dye rejection and effluent quality, but also retain most salt ions [27–29]. This generates an osmotic pressure difference, requiring the use of high trans-membrane pressures [4,15,19,27–30]. A UF membrane with a smaller pore size around 1 nm that can effectively reject dyes but not salts could allow low pressure operation with high effluent quality. Furthermore, the effluent that already contains reclaimed salt can be

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reused directly, providing potential cost savings up to 5–10$/m^3 wash water [31].

In each of these wastewater treatment applications, membrane fouling remains the key challenge to overcome [6–8]. Fouling occurs due to the adsorption and accumulation of feed components on the surface and inside the pores of membranes, leading to significant decline in flux and overall performance. Fouling results in lower productivity, higher energy use, membrane cleanings using harsh chemicals, and shorter membrane life. In most domestic and municipal wastewater treatment applications, the organic macromolecules in the feed, termed effluent organic matter (EfOM), are the major contributors of membrane fouling [6–8,32–35]. EfOM typically contains polysaccharides, proteins, humic acid, fulvic acids, amino acids and fatty acids [5,7,13,36–39]. The presence of certain cations such as calcium worsens membrane fouling by forming complexes with polysaccharides and humic acid in EfOM [6,40]. Industrial wastewater streams may also contain these foulants, but their composition is diverse and application dependent. Oil emulsions, fatty acids and grease are common foulants in wastewater and produced water streams from oil and natural gas production, petrochemical processing, and petroleum refining [16–18]. Textile wastewater streams also contain these components, though their composition is even more complex and hard to mimic [19,41,42].

Engineering the membrane surface chemistry to resist the adsorption of common foulants can proactively control fouling, and enable more energy efficient, stable membrane operation without the downtime, maintenance and chemical use associated with cleaning procedures. Zwitterions, functional groups featuring equal numbers of positively and negatively charged moieties connected by covalent bonds, prevent fouling due to their high degree of hydration, which makes foulant adsorption energetically unfavorable [43–54]. Membranes with zwitterion-functional surfaces created by post-functionalization methods can resist fouling by proteins [55–60] and oil suspensions [61]. These methods, however, require additional processing steps, increasing manufacturing complexity and costs. Furthermore, studies with more complex feeds, a broader range of relevant foulants, and realistic feeds are limited.

Recently, we have reported fouling resistant membranes whose selective layers consist of self-assembling random zwitterionic copolymers that self-assemble to form bicontinuous networks of nanochannels [62,63]. Unlike other studies where zwitterions are utilized exclusively to improve fouling resistance [55–61,64–75], these membranes rely on the microphase separation of the zwitterionic copolymer to form hydrophilic nanochannels that act as pores. Thus, they derive not only their fouling resistance but also their permeability and selectivity from the self-assembly of the designed zwitterionic amphiphilic copolymer. These membranes exhibit size-based selectivity with a size cut-off of ~ 1 nm, corresponding to a MWCO of ~ 1000 Da. Two of these membranes exhibited complete resistance to irreversible protein fouling: membranes prepared from poly(trifluoroethyl methacrylate-*random*-sulfobetaine methacrylate) (PTFEMA-*r*-SBMA, termed PT:SBMA) and from poly(trifluoroethyl methacrylate-*random*-2-methacryloyloxyethyl phosphorylcholine) (PTFEMA-*r*-MPC, termed PT:MPC). PT:MPC showed no flux decline even during the filtration of the foulant solution during the 24-h dead-end filtration experiment.

This unprecedented degree of fouling resistance with synthetic protein solutions is extremely promising, but does not necessarily predict resistance to other foulants or more complex feeds necessary for the use of this new technology in realistic applications such as wastewater treatment. Indeed, membrane fouling is strongly affected by the composition of the feed. Resistance to fouling by one type of foulant (e.g. bovine serum albumin, BSA) often does not predict resistance to fouling by another (e.g. other proteins, natural organic matter, oil, dyes…) [76]. Furthermore, the presence of multiple components in the feed can drastically change how fouling occurs. The most common example is the significant enhancement in humic acid and alginate fouling in the presence of Ca^{2+} ions, especially if the membrane surface contains carboxylate groups [31,37,77–79]. Tests with mixtures of foulants often exhibit features not observed or predicted from single foulant tests [37,76,80–82]. Interactions between different feed components can affect not only fouling but also rejection [12,81]. These challenges are further amplified during the treatment of actual wastewater streams that contain a complex and constantly changing mixture of components [14–16,81,83,84]. Therefore, previously reported tests with these zwitterionic membranes cannot accurately predict their performance in realistic applications and clearly assess the applicability of these novel membranes to the treatment of complex wastewater streams.

In this work, we investigated the performance of these two zwitterionic membranes in treating municipal and industrial wastewater streams. To assess their potential in treating municipal wastewater, we studied their fouling resistance to organic foulants commonly found in EfOM, as single components and as a mixture. These membranes showed exceptional resistance to fouling, exhibiting no irreversible flux decline after 24-h dead-end filtration tests. We also documented their chemical stability to common cleaning solutions and chlorine. To explore their potential in industrial wastewater treatment, we performed 7-day fouling tests with oil emulsions. In these tests, one membrane showed no decline in flux even during the filtration of the oil emulsion, an unprecedented degree of fouling resistance. Finally, we filtered real wastewater samples from a textile dyeing plant in Turkey. We observed no irreversible flux decline after the test, and high removal of dyes and colored substances combined with low salt rejection. This could potentially provide an effluent for reuse with minimal additional treatment and without the addition of salts, leading to significant cost savings in the long run. This study demonstrates the promise of these novel membranes for a broad range of challenging wastewater streams including municipal, oil industry and textile wastewater.

2. Experimental

2.1. Materials

Azobisisobutyronitrile (AIBN), 4-methoxyphenol (MEHQ), sulfobetaine methacrylate (SBMA), 2-methacryloyloxyethyl phosphorylcholine (MPC), bovine serum albumin (BSA, 66.5 kDa), phosphate buffered saline (PBS) packets (0.01 M, pH 7.4), humic acid (HA), sodium alginate (SA, ultra-low viscosity 5–40 cP), octanoic acid, brilliant blue R, chicago sky blue 6B, and calcium chloride ($CaCl_2$) were purchased from Sigma Aldrich (St. Louis, MO). 2,2,2 trifluoroethyl methacrylate (TFEMA) was obtained from Scientific Polymer Products Inc. (Ontario, NY). Trifluoro ethanol (TFE), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), isopropanol (IPA), methanol (MeOH), ethanol, hexane, lithium chloride (LiCl) and basic activated alumina were purchased from VWR (West Chester, PA). Deuterated dimethyl sulfoxide (DMSO-d_6) was obtained from Cambridge Isotope Laboratory (Tewksbury, MA). DC193 surfactant and soybean oil were obtained from Dow Chemicals (Providence, RI) and the supermarket, respectively. All chemicals and solvents were reagent grade and used as received except TFEMA, which was purified by passing through a column of basic activated alumina. Poly(vinylidene fluoride) (PVDF) 400R ultrafiltration membranes purchased from Nanostone Water (Eden Prairie, MN) were used as the base membrane. Poly(ether sulfone) (PES) 1 kDa molecular weight cut-off (MWCO) membranes (Sartorius), purchased from Fisher Scientific Inc (Pittsburgh, PA), were used as the controls. Ultrapure deionized water supplied by Biolab 3300 RO, a building-wide Reverse osmosis/Deionized water (RO/DI) purification unit by Mar Cor Purification was used for all the experiments.

2.2. Synthesis of zwitterionic copolymers

2.2.1. Synthesis of PTFEMA-r-SBMA and PTFEMA-r-MPC copolymers

Random copolymer of TFEMA and SBMA monomers, poly(trifluoroethyl methacrylate-*random*-sulfobetaine methacrylate) (PTFEMA-

r-SBMA, termed PT:SBMA) was synthesized by free radical polymerization (FRP) using a previously published procedure with small modifications [62]. Lithium chloride (0.1 g) was dissolved in 80 ml of dimethyl sulfoxide by stirring in a round-bottomed flask. Four grams of sulfobetaine methacrylate (SBMA) was added to the flask and dissolved in the solution by stirring, followed by TFEMA (six grams) and AIBN (0.01 g). The flask was sealed with a rubber septum, purged with nitrogen for 20 min, and placed in an oil bath at 70 °C with stirring. After 20 h, the flask was removed from the oil bath. 0.5 g of 4-methoxyphenol (MEHQ) was added to the flask to terminate the reaction. Copolymer was precipitated in a 50:50 mixture of ethanol and hexane. The product was vacuum filtered and remaining solvent and monomers were extracted by stirring the polymer in methanol bath twice for at least 8 h. The final product was dried in the vacuum oven overnight at 50 °C. The copolymer composition was determined by ^{1}H NMR spectroscopy.

Random copolymer of TFEMA and MPC monomers, poly(trifluoroethyl methacrylate-*random*-2methacryloyloxyethyl phosphorylcholine) (PTFEMA-*r*-MPC, termed PT:MPC) was also synthesized by FRP using a similar procedure [63]. TFEMA was passed through a column of basic activated alumina to remove the inhibitor. Three grams of MPC was dissolved in 65 ml of ethanol by stirring in a round-bottomed flask. TFEMA (seven grams) and AIBN (0.01 g) were added. The flask was sealed with a rubber septum, purged with nitrogen for 20 min, and placed in an oil bath at 70 °C with stirring. The flask and oil bath setup was covered with aluminum foil as the MPC monomer is reported to be somewhat light sensitive. After 20 h, the flask was removed from the oil bath. 0.5 g of 4-methoxyphenol (MEHQ) was added to the flask to terminate the reaction. Copolymer was precipitated in tetrahydrofuran. The product was vacuum filtered and remaining solvent and monomers were extracted by stirring the polymer in a tetrahydrofuran bath twice for at least 8 h. The final product was dried in the vacuum oven overnight at 50 °C. The copolymer composition was determined by ^{1}H NMR spectroscopy.

2.2.2. Large scale copolymer synthesis

We also synthesized larger batches of PT:SBMA and PT:MPC copolymers. PT:MPC copolymer was synthesized as described above, while PT:SBMA copolymer synthesis was optimized by making slight modifications to the above procedure. We used 100 g of total monomers in the reaction mixture. 60 g of TFEMA and 40 g of SBMA were dissolved in 200 ml of trifluoroethanol (TFE) by stirring in a round-bottomed flask. Trifluoroethanol was used instead of dimethyl sulfoxide (DMSO) because the monomers and the copolymer showed better solubility in this solvent, which allowed us to use only one-fourth of the amount of solvent compared with DMSO. 0.1 g of AIBN was added and the flask was placed in an oil bath at 70 °C with stirring. After 24 h, the copolymer was precipitated in isopropanol. The product was vacuum filtered and remaining solvent and monomers were extracted by stirring the polymer in an isopropanol bath twice for at least 8 h. The final product was dried in the vacuum oven overnight at 50 °C. The yield was 85%, much higher than small scale batches (10 g). The copolymer composition was determined by ^{1}H NMR spectroscopy.

2.3. Membrane preparation

Thin film composite (TFC) membranes were prepared by coating selective layers of zwitterionic copolymers on porous supports as described previously [62,63]. Briefly, PT:SBMA and PT:MPC were dissolved in trifluoroethanol (TFE) to form 10% (w/v) and 12% (w/v) solutions, respectively. Solutions were filtered through a 1 μm glass fiber syringe filter (Whatman) and degassed by placing the sealed vial in an oven at 50 °C for at least an hour. The copolymer solution was coated onto PVDF 400 R ultrafiltration membranes (Nanostone Water) using a doctor blade set at a gate size of 25 μm, followed by 0 and 10 min solvent evaporation for PT:SBMA and PT:MPC membranes, respectively. Membranes were immersed in isopropanol for 20 min to precipitate the copolymer. Thereafter, all membranes were stored in deionized water until further use. The coating solvent partially swells the support membrane, and the coating layer slightly penetrates into the surface pores of the support before being solidified upon immersion into water. This leads to a stable layer resistant to delamination, anchored both mechanically and through intermolecular interactions. Selective layer thickness and morphology was characterized by Scanning Electron Microscopy (SEM) using a Phenom G2 Pure Tabletop SEM operated at 5 kV. Membrane samples were air dried, then freeze-fractured using liquid nitrogen and sputter coated with gold-palladium before cross-sectional examination with the SEM.

2.4. Filtration experiments

Filtration experiments were performed on 25 mm diameter circular membranes using a 10 ml Amicon 8010 stirred, dead-end filtration cell (Millipore) with an effective filtration area of 4.1 cm^2. The cells were continuously stirred to minimize concentration polarization, and were attached to a 1 gallon reservoir. DI water was passed through the membranes at a transmembrane pressure (TMP) of 20 psi (1.4 bar) until the flux remained stable for at least a half hour. Permeate weight was measured using a Scout Pro SP401 balance connected to a Dell laptop, which automatically takes measurements at 30 s intervals using TWedge 2.4 software (TEC-IT, Austria). The measured volume can vary by 1–2 droplets (0.05–0.1 ml) at each data point.

Flux is defined as the flow rate through the membrane normalized by membrane area. Permeance is a membrane property that normalizes the flux to account for operating conditions, and is obtained by

$$L_p = \frac{J}{\Delta p} \quad (1)$$

where L_p is the permeance of the membrane (L m^{-2} h^{-1} bar^{-1}), J is the water flux across the membrane (L m^{-2} h^{-1}), and Δp is the trans-membrane pressure (bar).

2.4.1. Single organic foulants

Fouling experiments were performed using the dead-end filtration equipment described above. First, deionized water was filtered through the membrane until the flux stabilized. The cell and reservoir were filled with the model foulant solution. Natural organic matter (NOM) solutions contained 1 g/L humic acid in deionized water (pH 7.2), with and without 10 mM calcium chloride ($CaCl_2$). $CaCl_2$ is documented to increase the fouling propensity of humic acid by forming complexes [6,40]. Polysaccharide fouling studies used 1 g/L sodium alginate in deionized water (pH 7.1). These solutions were filtered with a TMP of 20 psi for 24 h. The cell was then rinsed several times with DI water and refilled with DI water to determine the reversibility of fouling. Protein and humic acid concentration in feed and permeate were quantified using UV absorbance at 280 nm and 255 nm respectively (Thermo Scientific Genesys 10 S). Salt concentration was determined using a conductivity meter. Sodium alginate concentration was determined by measuring the Chemical Oxygen Demand (COD) using 20–1500 mg/L Hach COD vials in a Hach DRB200 dry thermostat reactor.

As a control, we performed the same tests on a commercial membrane with similar pore size, a poly(ether sulfone) (PES) membrane (Sartorius) with a nominal molecular weight cut-off (MWCO) of 1000 Da. Its size cut-off is comparable to PT:SBMA and PT:MPC TFC membranes as documented in previous studies [62,63].

2.4.2. High concentration mixture of EfOM components

In order to measure the fouling resistance of these membranes to mixed EfOM components, we prepared a feed based on a previously published study on EfOM fouling in wastewater treatment systems [85], containing a mixture of proteins, polysaccharides, humic acid and fatty acids [5,13,32–36]. To challenge the membranes under a worst case

scenario, we increased all concentrations used in this study by an order of magnitude. Stock solutions were prepared by dissolving BSA in 0.01 M PBS solution (pH 7.4), and alginate, humic acid and octanoic acid in deionized water at a concentration of 1 g/L each. Subsequently, these were mixed together in equal volumes (250 ml each) to form a 1 g/L total concentration of organic foulants. The solution was mixed together at least overnight to ensure complete dissolution. Then, the ionic strength of the stock solution was adjusted by adding 0.5 mM $CaCl_2$ and 9.5 mM NaCl. The pH was adjusted to 6.5 ± 0.1 by adding small amounts of HCl or NaOH as necessary.

Fouling tests were performed in crossflow mode using an acrylic crossflow cell assembly (CF016A, Sterlitech) with an active membrane area of 2.6 cm^2 and a slot depth of 0.23 cm. The crossflow velocity was set to 0.09 m/s by using a flow rate of 480 ml/min, corresponding to a Reynolds number of 429 to ensure laminar flow conditions. First, deionized water was filtered through the membrane at a TMP of 20 psi (1.4 bar) until the flux was stable. A 100 mg/L of an aqueous solution of a negatively charged dye, Brilliant Blue R (1.1 nm in diameter), was filtered through the membrane by applying a TMP of 20 psi (1.4 bar), to check for defects, followed by rinsing by filtering deionized water for at least 2.5 h. Thereafter, the foulant mixture was filtered for at least 6.5 h at a TMP of 20 psi (1.4 bar). The feed was switched to DI water, which was run through the system at a TMP of 2 psi for 5 min to rinse the membrane. Then the TMP was raised back to 20 psi and water flux was measured.

2.4.3. Water analysis

Conductivity and total dissolved solids (TDS) was determined using a conductivity meter (VWR Traceable). Turbidity was determined by using a turbidity meter (HF Scientific inc. MicroTPW Turbidimeter). Organic removal was determined by measuring Chemical Oxygen Demand (COD) using 20–1500 mg/L Hach COD vials and a Hach DRB200 dry thermostat reactor. Removal of small aromatic organics was determined by UV_{254} values measured by filtering the solutions with a 0.45 μm filter and measuring the UV absorbance at 254 nm (Thermo Scientific Genesys 10 S). Total suspended solids (TSS) was determined by drying a glass fiber filter (Whatman, 1 μm pore size) in a vacuum oven at 105 °C, obtaining the dry weight, filtering 20 ml of each solution, and drying it again until its weight stabilized [18]. The TSS value was calculated using the change in the weight of the filter.

2.4.4. Membrane cleaning

In order to characterize the chemical stability of the membranes, we weighed and soaked membrane samples in five salt solutions (5, 10, 20, 30 and 58.44 g/L NaCl) and four buffers set to selected pH values (pH 4, 7, 10 and 13) for three hours. After soaking, the membrane was rinsed with deionized water a few times, dried overnight, and weighed again to calculate the change in weight.

To characterize the stability of membrane morphology upon exposure to solutions of a wide range of pH values, we characterized the copolymer coatings using Attenuated Total Reflection Fourier transform infrared (ATR-FTIR) spectroscopy. FTIR spectra were obtained using JASCO FT/IR-6200 type A spectrometer in absorption mode with a triglycine sulfate (TGS) detector. Membrane samples, 1 cm^2 in area, were air-dried overnight prior to FTIR analysis. Baseline-corrected spectra were collected over a range of 600–4000 cm^{-1} at 4 cm^{-1} resolution and averaged over 128 scans to improve the signal-to-noise ratio. Spectra were processed using the Spectra Manager II software (JASCO). Membrane samples were soaked for 24 h in buffers set to four selected pH values (4, 7, 10 and 13), and the membrane surface morphology was analyzed by using ATR-FTIR spectroscopy.

To characterize the chemical stability upon exposure to common chemical cleaning agents, membrane performance was measured after soaking membrane samples in aqueous solutions of citric acid (0.01 M, pH 2), sodium hydroxide (NaOH, 0.01 M, pH 12), or 1000 ppm sodium hypochlorite (at room temperature or at 35 °C in a water bath) for three hours. Each solution was freshly prepared and adjusted to pH 7.1 by the addition of small amounts of HCl. The concentration of chlorine in the solution was confirmed using chlorine test strips. A long exposure test was also performed by soaking membrane samples in 1000 ppm sodium hypochlorite for one week. In each case, water permeance, solute retention and fouling resistance was measured before and after soaking under the five chemical cleaning conditions mentioned above. Based on previous research on PT:SBMA-coated and PT:MPC-coated membranes which showed that these membranes exhibit a size cut-off of ~ 1 nm [62,63], Chicago Sky Blue 6B (0.879 nm in diameter, one of the dyes right around the cut-off) was filtered at a TMP of 20 psi (1.4 bar). The first ml of filtrate was discarded and the following ml of filtrate was used to calculate rejection by measuring the percentage change in concentration of the feed and the permeate defined as

$$R = \frac{100(C_f - C_p)}{C_f} \quad (2)$$

where R is the solute rejection (%), C_f is feed concentration (mg/L), and C_p is the permeate concentration (mg/L). Dye concentrations in the feed and permeate were measured using UV–Vis spectroscopy (Thermo Scientific Genesys 10S). 1 g/L BSA in PBS was used as the foulant.

2.4.5. Oil emulsion

A 1.5 g/L oil-in-water emulsion (9:1 ratio of soybean oil: DC193 surfactant) [62,86] was used to simulate oily wastewaters generated from various industries that include food production, petroleum refining, hydrocarbon processing and other industrial wastewaters with high oil content [16–18,87]. While these streams all contain different types of oil, we selected soybean oil because it is commercially available with consistent properties, allowing us to acquire reproducible data. Similar compositions based on soybean oil were used previously by other groups for the same reason [86,88,89]. Using the same emulsion formulation allowed us to generate data that can be compared with these other studies. These tests were performed using the dead-end filtration procedure described in Section 2.4.1, but the foulant was filtered for 1 week instead of 24 h.

2.4.6. Real textile wastewater

Textile wastewater samples were received from a textile dying plant in Denizli, Turkey. The sample was taken from a reactive dye bath containing Reactive Orange S3R, Reactive Deep Red SB6, and Remazol Ultra Navy Blue as well as salts, soda and caustic. Fabrics are dyed by immersion into this bath in a batch process, and then rinsed with various solutions. The wastewater stream used in these experiments was the used dye bath, undiluted with the rinse baths.

These tests were performed in a dead-end system similar to those described in Section 2.4.1. First the membrane was compacted by permeating deionized water at 3 bar (43.5 psi) for 2 h. Real textile wastewater samples were passed through these membranes for at least 7 h. After filtering the foulant solution for the selected permeate amount, filtration was stopped, the retentate was emptied and analyzed. The cell was filled with DI water and the membranes underwent a physical cleaning similar to the water rinse described above, by stirring the cell at 250 rpm for 15 min. Any difference between the water permeance after this stage and the initial water permeance was considered to be associated with irreversible fouling.

All testing was performed at 2 bar (or 29 psi) and with a volume reduction factor of 2. Color retentions were determined by measuring UV absorbance at three wavelengths: 436 nm, 525 nm, and 620 nm (Varian Cary 100). Conductivity was determined using a conductivity meter (Hach Sension 378) and turbidity was determined using a turbidity meter (Hach 2100). Total Organic Carbon (TOC) was measured using a Schimadzu 5000 A TOC analyzer using the 680 °C combustion – catalytic oxidation method. A commercial proprietary TFC 2 kDa membrane from GE-Osmonics (UF-GH), which is in the pore size range

typically used for treating textile wastewater effluents [90–92], was used as the control. This membrane was pre-treated with an initial chemical cleaning with nitric acid (pH = 3 for 15 min) followed by NaOH (pH = 10 for 15 min) to stabilize its performance.

3. Results and discussion

3.1. Membrane water permeance

Two membranes featuring different types of zwitterionic groups, identified by their promising fouling resistance in previous studies that also include extensive characterization of their chemistry, microphase separation, and surface and morphological properties, were used in this work [62,63]. Each membrane was prepared by coating a porous support membrane with the zwitterionic copolymer to form a ~ 1 μm-thick selective layer [62,63]. PT:SBMA featured sulfobetaine zwitterionic groups, whereas PT:MPC contained phosphorylcholine groups. Both copolymers were synthesized using a simple, highly scalable free radical copolymerization method using commercially available monomers. The synthesis method led to copolymers with highly reproducible compositions, and was easily scaled up to 100 g scale (see Supporting information). This demonstrates the promise of the membrane technology for large scale applications.

The water permeances of PT:SBMA and PT:MPC TFC membranes were 5.83 ± 1 L m^{-2} h^{-1} bar^{-1} and 4.74 ± 0.8 L m^{-2} h^{-1} bar^{-1}, respectively. Previous studies have shown that these membranes have rejections comparable with a commercial poly(ether sulfone) (PES) membrane with a nominal molecular weight cut-off (MWCO) of 1 kDa (Sartorius) [62,63]. The water permeance of this membrane, which was used as a benchmark in this study, was 2.55 ± 0.1 L m^{-2} h^{-1} bar^{-1}, significantly lower than PT:SBMA and PT:MPC TFC membranes. This MWCO is on the lowest end of available pore sizes for UF membranes. This is expected to lead to significantly better effluent quality by removing contaminants of smaller size compared with higher MWCO UF membranes commonly used in these applications, especially for wastewaters that contain organic contaminants such as dyes.

3.2. Fouling by single EfOM components

PT:SBMA and PT:MPC TFC membranes show no irreversible fouling in 24-h experiments with protein solutions [62,63]. In this study, we investigated the fouling resistance of these membranes to a broader range of organic foulants found in EfOM in municipal wastewater. These experiments were performed in dead-end mode, a worst case scenario for fouling. We selected foulants representing other problematic EfOM components: polysaccharides and natural organic matter (NOM) [5,7,13,36–39]. Polysaccharides, especially alginates, are a component of extracellular polymeric substances (EPS), the major fouling component in the filtration of biological wastewater feeds in industry [83]. They are also used as thickeners and stabilizers in food, textile, and pharmaceutical industries [93]. NOM, especially humic acid, is a degradation product of lignin, carbohydrates and proteins that leaches out from soil into municipal wastewaters [94]. Model polysaccharide and NOM foulant solutions comprised 1 g/L alginate and 1 g/L humic acid in deionized water, respectively. Fouling by humic acid is reported to be intensified in the presence of calcium salts due to the formation of complexes [6,40], therefore humic acid was filtered along with 10 mM of $CaCl_2$ and a mixture of 0.5 mM $CaCl_2$ and 9.5 mM NaCl. All tests were performed at a TMP of 20 psi for a 24-h period (Fig. 1).

PT:SBMA and PT:MPC TFC membranes retained a higher flux than the commercial membrane throughout all experiments (Fig. 1). They also completely resisted irreversible fouling with all four single-foulant solutions (Fig. 2). The water flux was fully recovered with a simple water rinse in every case. In comparison, the commercial PES membrane with a similar pore size showed irreversible flux declines between 40–48% (Fig. 2). All three membranes exhibited high rejections of these organic compounds (Table 1). Humic acid with and without salts was removed by 98–99% by all three membranes. The two zwitterionic membranes both exhibited alginate retentions of 98% whereas the commercial membrane removed alginate by 94%.

3.3. High concentration mixture of EfOM components

While most new membranes are tested with simplified, single-component feeds, real wastewater streams are complex mixtures of multiple foulants. Interactions between these different components with each other and with the membrane surface may lead to behaviors that are not predicted by single-foulant tests [35,85]. We aimed to address this concern by preparing a high concentration mixture of common organic foulants present in municipal wastewater streams. We selected a mixture of polysaccharides, NOM, proteins and fatty acids that has previously been used to characterize the fouling of membranes in the context of municipal wastewater treatment and the filtration of secondary wastewater effluent [32,35,85]. We chose to challenge these membranes with a 10 times more concentrated mixture of these foulants than reported previously [85], with a feed solution containing 250 mg/L each of alginate, humic acid, BSA, and octanoic acid with 0.5 mM $CaCl_2$ and 9.5 mM NaCl, set to pH 6.5 ± 0.1. This foulant mixture was dark brown in color, with turbidity and TSS in the typical range for municipal wastewaters (Table 2) [95]. The COD and UV_{254} values indicated a much higher organic content than typical municipal wastewaters [32,34,35]. The conductivity was comparable to or higher than real municipal wastewater streams [32,35].

Using this feed, membranes were tested in a cross-flow system, which more closely mimics operation in the field. PT:SBMA and PT:MPC TFC membranes both exhibited complete rejection of suspended solids and high turbidity removal (Table 2). They also exhibited high rejections of organic solutes, with > 80% reduction of COD and 94–96% removal of aromatic organic compounds evidenced by UV_{254} measurements. These zwitterionic membranes also showed low retention of salts, with conductivity removal below 11%. Low salt retention allows the use of lower pressures and also prevents issues of scaling during membrane operation.

The commercial PES 1 kDa membrane showed similar removals of turbidity and suspended solids, but lower rejections of organics (Table 2). Conductivity measurements showed 85% rejection of salt and dissolved solids, significantly higher than zwitterion-containing membranes. Salt removal can arise from ions getting retained in the fouling layer owing to Ca^{2+} forming complexes with humic acid and/or sodium alginate [6,40], or due to electrostatic interactions with charged groups on the PES surface originating from surface treatments to improve wettability and prevent fouling. Many low MWCO UF membranes also have charged surfaces to improve their measured pore size, as electrostatic interactions can aid in the retention of charged small molecules. This may also have contributed to the high salt rejection of this membrane. In contrast, the zwitterionic membranes described here have a zero net charge. Their selectivity relies on size exclusion rather than electrostatic interactions. This leads to only minimal rejection of salt ions, which are much smaller in size than the self-assembled nanochannels that form the permeation pathways, combined with a comparable or even better rejection of organic compounds [62,63].

In addition to exhibiting high organic removal, the two zwitterionic membranes tested showed excellent fouling resistance. The flux declined by only 8–13% during the filtration of this challenging stream for 6.5 h (Fig. 3). Water flux was fully recovered to values within the error margin upon switching back to pure water as the feed. In contrast, the commercial PES membrane exhibited a 60% flux loss during the filtration of the foulant mixture. Even after a water rinse, the flux was 45% lower than its initial value. This demonstrates that both zwitterionic copolymers exhibited much better resistance to fouling than the commercial alternative.

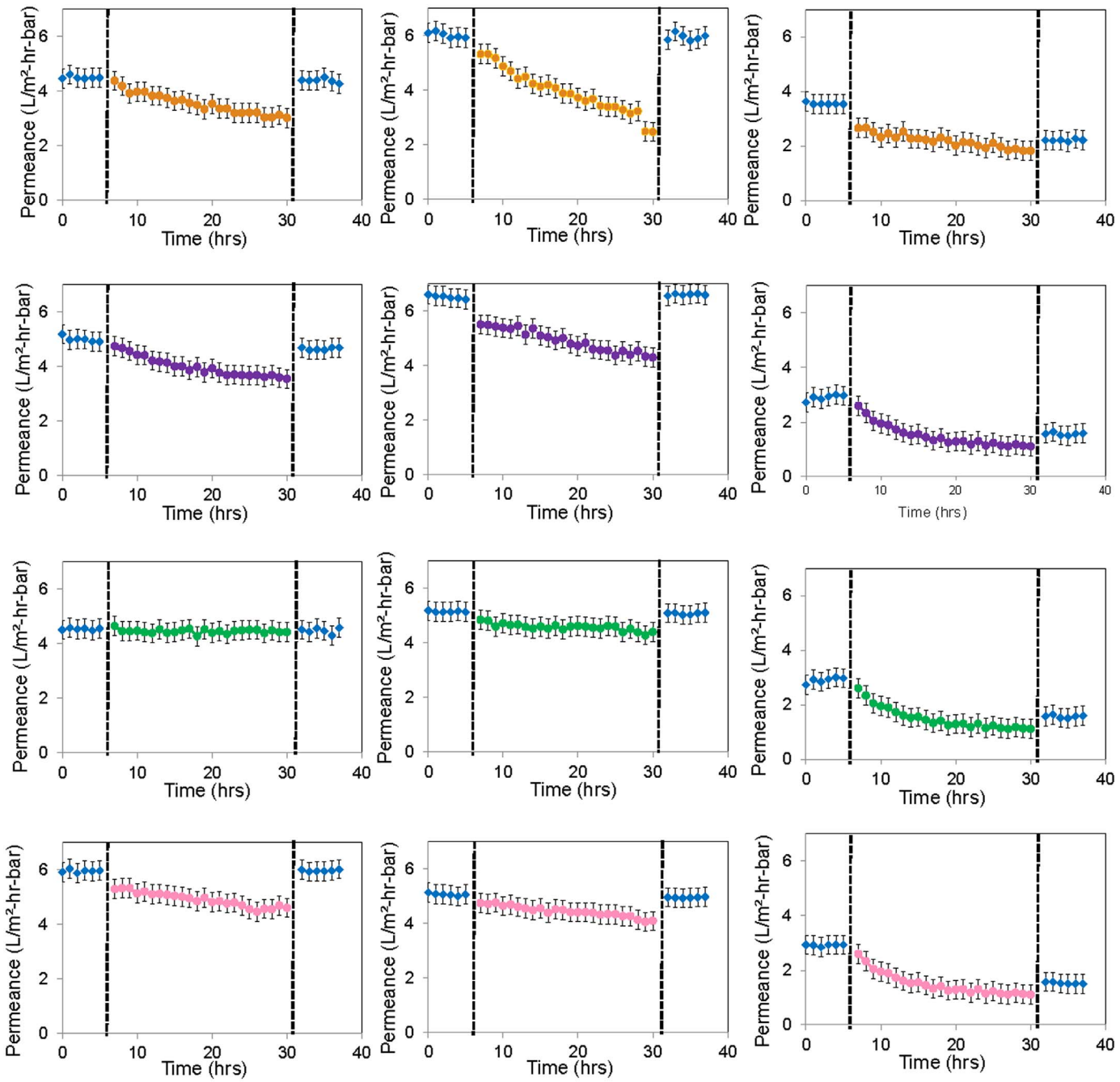

Fig. 1. Fouling resistance of zwitterionic copolymer TFC and PES 1 kDa membranes to single EfOM components – alginate (top row), humic acid (second row), humic acid/$CaCl_2$ (third row) and humic acid/$CaCl_2$/NaCl (bottom row) mixtures. Plots show initial water permeance (blue; to the left of dashed lines), foulant solution permeance (various colors; between dashed lines), and water permeance after rinse (blue; to the right of dashed lines) for PT:SBMA (left column) and PT:MPC (middle column) TFC membranes and commercial PES 1 kDa (right column) membrane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

3.4. Chemical resistance to disinfection and cleaning solutions

Membranes are routinely exposed to chemicals that are added to kill microorganisms in feed water to prevent microbial growth, or during disinfection and cleaning processes. Commercial membranes, especially polyamide [96] and poly(vinylidene fluoride) [97,98] membranes, are sensitive to common cleaning and disinfection agents such as chlorine. This leads to performance loss and can chemically alter the membrane chemistry. Thus, new membrane materials must be chemically stable in contact with common cleaning agents.

To characterize chemical stability, we first tested if any weight loss was observed upon soaking PT:MPC- and PT:SBMA-coated membranes in salt solutions (5, 10, 20, 30 and 58.44 g/L of NaCl) and buffers set to four selected pH values (pH 4, 7, 10 and 13) for three hours. Both zwitterion-containing membranes showed < 3% change in weight, below the detection limit (see Supporting information). The surface chemistry of membranes soaked for 24 h in buffers set to selected pH values (4, 7, 10 and 13) was also analyzed using ATR-FTIR spectroscopy. Fig. 4 displays the FTIR spectra for PT:SBMA-coated membrane soaked in various pH solutions for 24 h. The spectrum shows that the chemical structure of the selective layer is intact and no adverse changes are visible upon exposure to these chemical solutions.

Chemical stability was characterized in more detail for three common cleaning/disinfection solutions: 0.1 M citric acid, 0.1 M

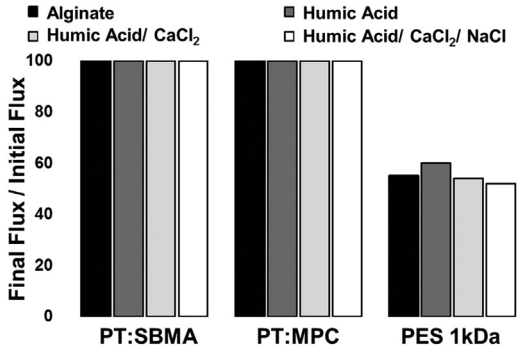

Fig. 2. Fouling of PT:SBMA and PT:MPC TFC membranes and a commercial membrane of similar pore size by EfOM components. Chart shows final flux/initial flux after 24 h filtration of 1 g/L solutions of organic foulants: alginate (black), humic acid (dark gray), humic acid with 10 mM $CaCl_2$ (light gray), and humic acid with a mixture of 0.5 mM $CaCl_2$ and 9.5 mM NaCl (white). In each case, PT:MPC and PT:SBMA TFC membranes show negligible irreversible flux loss after exposure to foulant solutions, whereas the commercial PES 1 kDa membrane shows significant irreversible flux loss.

Table 1
Rejections of single effluent organic matter components by zwitterionic copolymer TFC membranes and a commercial membrane of similar pore size.

Organic foulant	PT:SBMA	PT:MPC	PES 1 kDa
Alginate, 1 g/L	98	98	94
Humic Acid, 1 g/L	99	99	99
Humic Acid, 1 g/L + 10 mM $CaCl_2$	99	99	99
Humic Acid, 1 g/L + 0.5 mM $CaCl_2$ + 9.5 mM NaCl	99	99	99

Table 2
Salt and organics removal in the treatment of a mixture of EfOM components.

Water quality parameters	Initial value	Rejection		
		PT:SBMA	*PT:MPC*	*PES 1 kDa*
Conductivity	5130 μS/cm	10.3%	7.2%	85.3%
TDS	2900 mg/L	10.5%	7.4%	86.5%
Turbidity	50 NTU	80.6%	82%	76.7%
TSS[a]	100 mg/L	100%	100%	93.0%
UV_{254}[b]	3.7 cm^{-1}	94.1%	96%	63.1%
COD	1065 mg/L	80.8%	85.7%	59.2%

[a] Measured by filtering solutions with 1 μm filter.
[b] Measured after filtering solutions with 0.45 μm filter.

NaOH, 1000 ppm aqueous sodium hypochlorite (pH 7.1). In each case, membranes were characterized by dead-end filtration tests to characterize water flux, selectivity (rejection of Chicago Sky Blue 6B, a dye close to the membrane size cut-off [62,63]) and fouling resistance to BSA before and after soaking in the cleaning solutions for three hours at room temperature. Additional tests were performed for the sodium hypochlorite solution, one at an elevated temperature (three hours at 35 °C) and one with extended exposure (seven days at room temperature). No significant change was observed in water permeance, dye rejection or fouling resistance (Table 3) of both membranes after cleaning except for a slight decline in the water permeance of PT:SBMA-coated membranes upon exposure to 0.1 M citric acid. This demonstrates that these two zwitterionic copolymer membranes are highly chemically resistant, and would retain their flux, selectivity and fouling resistance upon exposure to most common cleaning solutions and to chlorinated water.

3.5. Fouling by oil emulsions

Large volumes of wastewaters containing oil and oil emulsions are

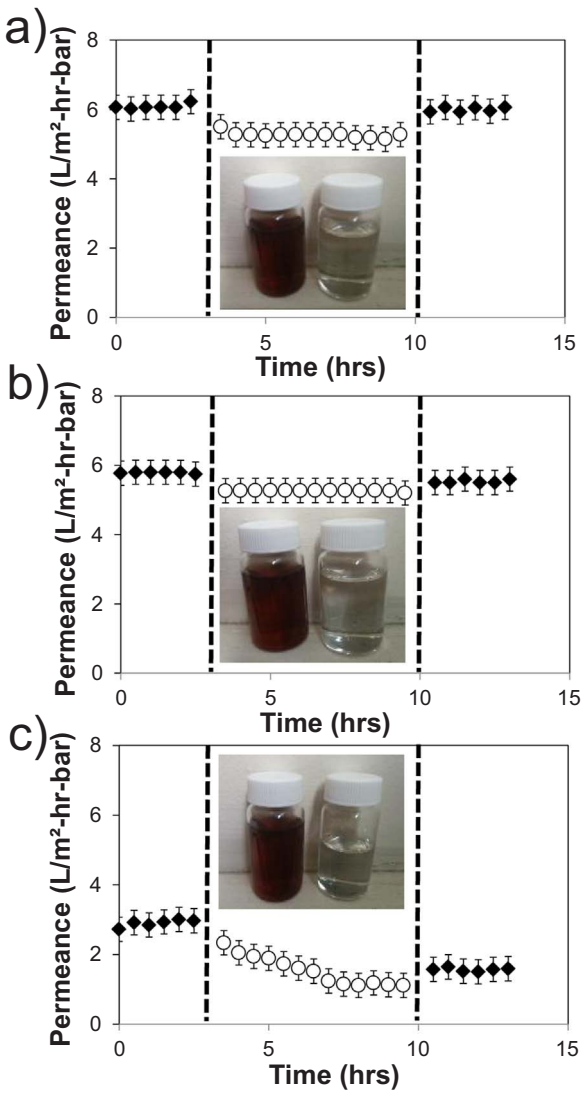

Fig. 3. Cross-flow filtration of a high concentration mixture of EfOM components. Plots show the initial permeance of water (black), followed by the permeance of the foulant mixture (white). Then, the membrane is rinsed with water, and water permeance is measured again (black). **a,** PT:SBMA and **b,** PT:MPC and **c,** Commercial PES 1 kDa membrane. Inset shows a photo of the feed (left) and permeate (right). PT:MPC and PT:SBMA membranes show negligible flux loss during and after the filtration of the foulant mixture, whereas the commercial PES 1 kDa membrane shows 45% irreversible flux loss.

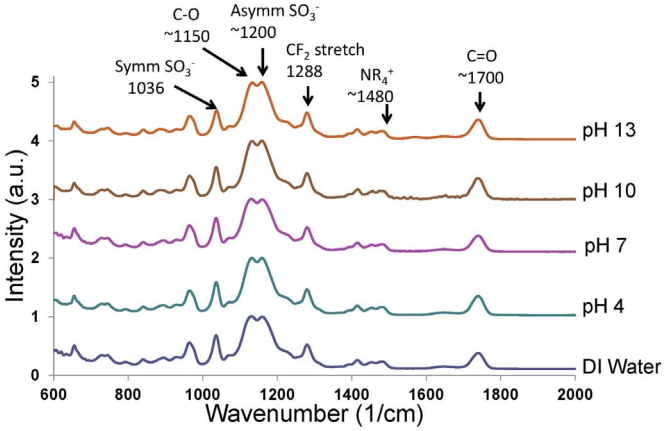

Fig. 4. FTIR characterization of PT:SBMA TFC membranes after soaking in various pH solutions for 24 h.

Table 3
Performance of zwitterionic copolymer TFC membranes upon exposure to various chemical cleaning solutions for 3 h.

Cleaning agents	Water permeance (L/m^2-h-bar)		Dye retention[a] (%)		Irreversible flux loss after fouling tests[b]	
	PT:SBMA	*PT:MPC*	*PT:SBMA*	*PT:MPC*	*PT:SBMA*	*PT:MPC*
Pristine membrane	6.4 ± 0.3	5.4 ± 0.3	95 ± 3	95 ± 3	< 1%	< 1%
1000 ppm Cl	6.4 ± 0.2	5.4 ± 0.3	95 ± 3	95 ± 3	< 1%	< 1%
1000 ppm Cl, 35 °C	6.4 ± 0.2	5.3 ± 0.2	96 ± 3	95 ± 3	< 1%	< 1%
1000 ppm Cl (1 week)	6.3 ± 0.3	5.3 ± 0.2	94 ± 2	94 ± 2	< 1%	< 1%
0.1 M NaOH	6.3 ± 0.2	5.4 ± 0.2	96 ± 2	95 ± 2	< 1%	< 1%
0.1 M citric acid	5.2 ± 0.3[c]	5.5 ± 0.3	96 ± 3	95 ± 3	< 1%	< 1%

[a] Dye: Chicago sky blue 6B.
[b] Foulant: 1 g/L BSA in PBS (pH 7.4). Full fouling curves in Supporting information.
[c] 22% loss in permeance upon cleaning.

produced by food, oil, natural gas, petroleum refining and textile industries, and their treatment is quite challenging [16–18]. In these streams, oil is typically present in three forms [16,99]: Free oil is in large droplets that eventually settle out of solution, and can be removed by conventional methods such as hydrocyclones. Emulsified oil is present as smaller stabilized droplets. Finally, dissolved oil comprises water-soluble components of oil such as phenol derivatives. Microfiltration membranes effectively remove free oil and some of the emulsified oil, whereas UF membranes effectively remove both [10,100–104]. The lower MWCO of the membranes discussed here may also potentially be able to remove some of the higher molecular weight dissolved oil components such as polyaromatic hydrocarbons (PAHs) from water streams associated with oil extraction and refining [102]. However, fouling issues are often very severe when membranes are exposed to feeds with high oil content [10,73,100–104]. This is likely the most significant factor that curtails the economic and technical feasibility of wider use of membrane processes in these applications.

To characterize the resistance of these membranes to fouling by oily feeds, we filtered a 1.5 g/L oil in water emulsion (9:1 ratio of soybean oil to DC193 surfactant) [62,86] in dead-end mode for seven days. Both zwitterionic membranes and the PES membrane produced clear permeates throughout the experiment. At the end of the test, the retentate in the cell appeared gray and highly concentrated. The commercial PES 1 kDa membrane showed an irreversible flux decline of 71% (Fig. 5). The PT:SBMA-coated membrane exhibited a flux decline of < 10% during oil filtration that was completely reversible by a pure water rinse. PT:MPC-coated membranes showed no decline in flux even during the filtration of the oily feed. This complete resistance to fouling is unprecedented, especially given the progressively increasing oil concentration in this long term dead-end experiment.

3.6. Filtration of real textile wastewater streams

While synthetic feeds are good tools for characterizing the performance of membranes in well-controlled systems, membrane behavior under realistic conditions can best be analyzed by treating real wastewater streams. As discussed earlier, the very low MWCO and low salt rejection of these newly developed membranes make them especially promising for treating textile wastewater, where low salt rejection combined with the removal of dyes and other organics can enable the reuse of the effluent for additional wash cycles.

Both PT:SBMA and PT:MPC TFC membranes showed 69% removal of total organic carbon (TOC) (Table 4). PT:SBMA removed 92–94% of color, whereas PT:MPC showed slightly lower color removal (81–84%). Both membranes also showed 93–98% turbidity removal. This indicates that these membranes successfully remove most of the dyes and organics and suspended solids in this wastewater stream. Conductivity removal corresponding to the retention of salts was very low, 1.3–4%. Low salt rejection allows the operation of the wastewater treatment process at lower pressures. This may potentially allow the reuse of the electrolyte-rich permeate stream as a rinse bath or as a dyeing bath with a simple, low-pressure membrane-based treatment scheme [90], especially if organics removal is improved further.

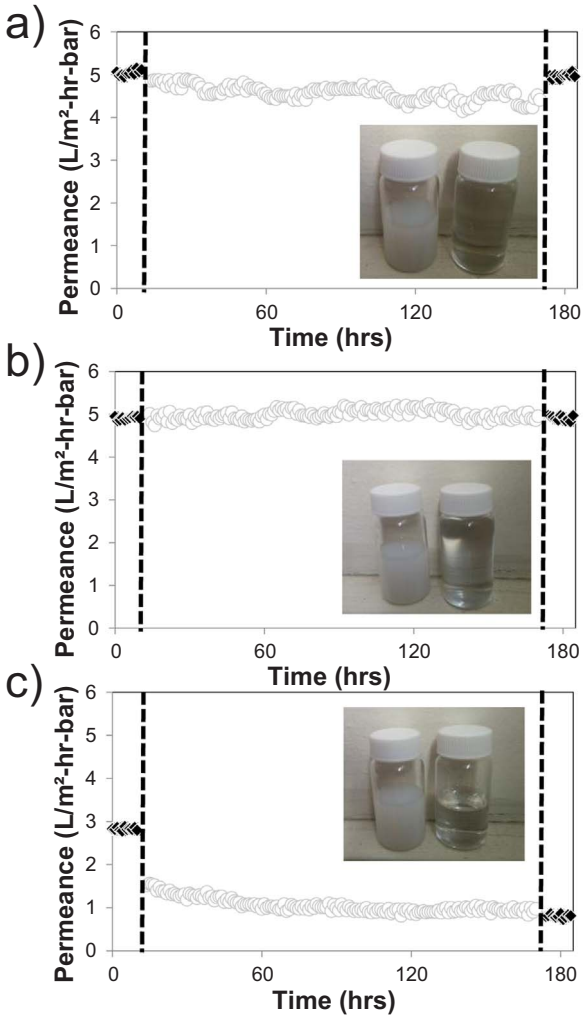

Fig. 5. Dead-end-filtration of oil emulsions through PT:SBMA and PT:MPC TFC membranes and commercial PES 1 kDa membrane. **a,b,c,)** Plots show the initial permeance of water (black), followed by the permeance of a 1500 mg/L oil-in-water emulsion (gray). Then, the membrane is rinsed with water several times, and water permeance is measured again (black). **a,** PT:SBMA and **b,** PT:MPC and **c,** commercial PES 1 kDa membrane. Inset shows a photo of the feed (left) and permeate (right). Both PT:MPC and PT:SBMA TFC membranes show negligible flux loss during and after exposure to foulant solutions, whereas the commercial PES 1 kDa membrane shows 71% irreversible flux loss after filtration.

Table 4
Rejection properties of zwitterionic copolymer membranes in treating real textile wastewater samples.

Performance parameters	Initial value	Rejection		
		PT:SBMA	*PT:MPC*	*Commercial TFC*
TOC	550–670 mg/L	69%	69%	72%
Turbidity	317–330 NTU	93%	98%	99.2%
Conductivity	73.5–98.5 mS/cm	4%	1.3%	13%
Color (436 nm)	3.37–3.61	94%	84%	95.2%
Color (525 nm)	2.91–3.09	93%	81%	94.5%
Color (620 nm)	0.37–0.41	92%	83%	93.7%

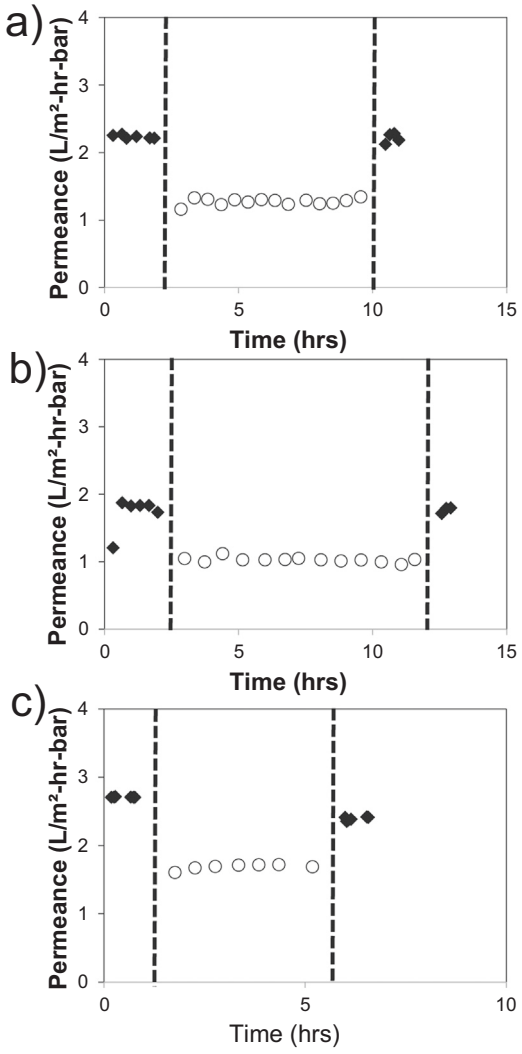

Fig. 6. Dead-end-filtration of real textile wastewater samples obtained from a textile dying plant in Turkey through PT:SBMA and PT:MPC TFC membranes and a commercial TFC 2 kDa membrane. Plots show the initial permeance of water (black), followed by the permeance of the real textile wastewater (white). Then, the membrane is rinsed by stirring with water in the cell, and water permeance is measured again (black). **a,** PT:SBMA **b,** PT:MPC and **c,** commercial TFC 2 kDa membrane. PT:MPC and PT:SBMA membranes show negligible flux loss after exposure to real textile wastewater, whereas the commercial TFC 2 kDa membrane showed 11% irreversible flux loss.

PT:SBMA and PT:MPC TFC membranes resisted fouling by this complex feed as well, showing only a slight decline in permeance during the filtration of the wastewater stream (11% and 23%, respectively) that was fully recovered upon physical cleaning by a water rinse (Fig. 6). The initial water flux and flux after cleaning are within error margins of each other. In either case, both membranes showed complete resistance to irreversible fouling by this real wastewater sample.

A commercial TFC 2 kDa membrane from GE-Osmonics (UF-GH) was used as the benchmark for this specific application based on previous studies of this specific membrane for textile wastewater treatment [90]. This membrane showed similar retentions for TOC (72%) and turbidity (99.2%) when compared to the zwitterionic membranes (Table 4). Color removal (93.7–95.2%) was similar to the PT:SBMA membrane, but somewhat higher than PT:MPC. On the other hand, this membrane retained conductivity by 13%, at a rate higher than the zwitterionic membranes. The flux during wastewater filtration was about half the clean water flux, as with the zwitterionic membranes. However, it could only be recovered by 89% after physical cleaning, whereas zwitterionic membranes exhibited 100% flux recovery. Furthermore, commercial TFC membranes are typically sensitive to chlorine-based disinfection and cleaning agents [96–98,105]. The superior fouling resistance and excellent chlorine resistance of the zwitterionic copolymer TFC membranes used in this study demonstrate their promise for this specific application.

4. Conclusions

In this work, we investigated the treatment of municipal and industrial wastewater streams using novel membranes featuring two self-assembling zwitterionic copolymers as selective layers. The membranes were prepared by coating these copolymers on a porous support to form a TFC membrane, and had effective MWCOs around 1000 Da as documented in previous studies [62,63]. These two membranes exhibited high rejections of organics and excellent resistance to fouling by organic foulants commonly found in municipal wastewater EfOM, as single components and as a mixture, exhibiting no irreversible flux decline. They also showed complete resistance to irreversible fouling by oil emulsions, common in various industrial wastewater streams, in week-long dead-end experiments. One membrane showed no flux decline during the filtration. This degree of fouling resistance is, to our knowledge, unprecedented in the field. These membranes were also tested in the treatment of real textile wastewater samples obtained from a textile dying plant in Turkey. Both zwitterionic copolymer membranes fully resisted irreversible fouling, and exhibited high rejections of dyes and colored substances while allowing salts to permeate, providing an effluent with high salt recovery. This offers the potential of low pressure operation and reuse of reclaimed salt. Finally, we documented that they were chemically stable, exhibiting no change in performance upon exposure to acidic, basic and chlorinated cleaning solutions. The excellent fouling resistance of these membranes, their chemical resistance, and their ability to effectively remove wastewater pollutants make them very promising for wastewater treatment applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2017.08.058.

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