Electrochemical Impedance Spectroscopy Study of Membrane Fouling and Electrochemical
Regeneration at a Sub-Stoichiometric TiO₂ Reactive Electrochemical Membrane

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Abstract

In this study, a novel substoichiometric TiO_2 ultrafiltration reactive electrochemical membrane (REM) was synthesized and used for electrochemical regeneration of membranes fouled by humic acid (HA) and polystyrene beads (PS). A non-invasive and non-destructive electrochemical impedance spectroscopy (EIS) characterization technique was used to spatially characterize fouling at the REM and data were successfully interpreted by a transmission line model. Based on these analyses, a chemical free electrochemical regeneration (CFER) scheme in backwash mode was developed. The CFER in anodic treatment mode recovered the flux of a HA fouled REM from 3.0% to between 76% and 99% of the initial flux over 5 continuous fouling/regeneration cycles. Full flux recovery of a PS fouled REM (fouling 31% to 38%) was achieved when using either cathodic or anodic CFER. By contrast, regeneration without an applied potential showed only partial flux recovery of 66% and 62% on HA fouled and PS fouled membranes, respectively. The operating cost of CFER was $\$0.04 \text{ m}^{-2}$ to $\$0.06 \text{ m}^{-2}$ per regeneration cycle, which is only 1.3% the cost of NaOH cleaning. Results suggest that the REM can provide an efficient and cost effective regeneration scheme that allows it to function in a diverse set of water treatment applications.

Nomenclature

CFER	Chemical Free Electrochemical Regeneration
EAOPs	Electrochemical Advanced Oxidation Processes
EIS	Electrochemical Impedance Spectroscopy
MWCO	Molecular Weight Cutoff
NOM	Natural Organic Matter
OCP	Open Circuit Potential
QRE	Quasi-Reference Electrode
REM	Reactive Electrochemical Membrane
SHE	Standard Hydrogen Electrode
TLM	Transmission Line Model
UF	Ultrafiltration

List of Symbols

Symbol	Name	SI Unit
$A_{electro}$	electroactive surface area	m^2
C_{dl}	double layer capacitance	F
$\bar{C}_{dl}$	surface normalized double layer capacitance	$\mu F \cdot cm^{-2}$
k	second order reaction rate	$M^{-1} \cdot s^{-1}$
J	membrane permeability	$LMH \cdot bar^{-1}$
R_{ct}	charge transfer resistance	Ohm
r	radius of pore	cm
t	Time	minute
V	Volume	mL
Y_0	capacitance constant	$F \cdot s^{\alpha-1}$

List of Greek Symbols

Symbol	Name	SI Unit
α	exponential factor	dimensionless
β	blocking law coefficient	unit depends on value of ϕ
ϕ	blocking law exponential factor	dimensionless
ρ	specific solution resistance	Ohm m
χ_I	ionic resistance	Ohm
λ	penetration depth	μm

1. Introduction

Membrane fouling significantly affects membrane filtration processes, as it leads to increased power consumption, reduced membrane life, and causes serious economic and operational challenges [1–5]. In order to recover fouled membranes, traditional membrane regeneration methods utilize physical and chemical cleaning protocols. Physical cleaning, such as periodic backwash, is able to partially regenerate the membrane using physical shear forces [6]. However, backwash treatments do not recover all of the membrane flux, and therefore chemical cleaning procedures are needed. The effectiveness of chemical cleaning is primarily hindered by mass transfer of the chemical reagents to the fouled membrane pores, which requires high concentrations of reagents (e.g., 0.5 M NaOH) in order to increase the driving force for mass transport [7]. In addition, the cost of chemical synthesis, shipment, storage, and disposal, and the environmental ramifications of the above make chemical cleaning methods undesirable from both the economic and environmental perspectives [8,9]. In order to address the challenges associated with membrane fouling and regeneration, we herein report on the synthesis of a novel ceramic, asymmetric, ultrafiltration (UF), reactive electrochemical membrane (REM) and the use of this REM to overcome membrane fouling through a chemical free electrochemical regeneration (CFER) method.

Electrochemical advanced oxidation processes (EAOPs) have emerged as a clean, cost effective, and promising technology for the destruction of recalcitrant organic compounds [10–15], and therefore this method should be amenable as an alternative to chemical cleaning methods for membrane regeneration. The only reagents needed during EAOPs are electrons, which eliminate the need for chemical addition. Organic foulants can be removed by hydroxyl radicals ($\text{OH}^\bullet$) produced from water oxidation on the anode surface (reaction 1), or oxidized through direct electron transfer reactions (reaction 2), where R is an organic compound [16].

In addition, membrane foulants can potentially be physically removed by electrostatic forces [18,19] and interaction with oxygen or hydrogen gas bubbles produced during water electrolysis reactions [20].

The integration of membrane filtration and EAOP into a single technology can provide efficient separations, oxidation of contaminants, and self-cleaning function. This combined process was recently realized through the development of a substoichiometric TiO₂ REM, which was applied to organic compound oxidation [23,24]. Substoichiometric TiO₂ is an ideal material for REM development, due to its long-term stability under both anodic and cathodic polarization [25,26], chemical inertness [27], and its high reactivity towards both inorganic [28] and organic [23,24] contaminants in wastewater streams. Substoichiometric TiO₂, known as Magnéli phases, has a general formula of Ti_nO_{2n-1} (3 ≤ n ≤ 20). The conversion of TiO₂ to Magnéli phases is achieved at temperatures above 1000 °C and in the presence of a reducing environment [27]. Magnéli phase materials are usually produced containing a mixture of compounds, with n typically between 4 and 6 [29]. The water treatment potential of the substoichiometric TiO₂ REM is immense, although few papers have investigated its potential [23,24,30], and therefore to our knowledge published studies have not been conducted that have documented fouling regeneration using a REM.

In this study, a substoichiometric TiO₂ UF membrane was developed and used as a REM in filtration mode. The objectives of this study were to (1) synthesize a durable and highly conductive substoichiometric TiO₂ membrane, (2) use a non-invasive EIS method to characterize membrane

fouling after various membrane fouling and regeneration events, and (3) establish a CFER method. The composition, porosity, and structure of the substoichiometric TiO_2 membrane were characterized using X-ray diffraction (XRD), Hg porosimetry, and scanning electron microscopy (SEM). The membrane fouling was induced by using model humic acid and polystyrene microspheres foulants. In order to understand the fouling modes, EIS spectra were interpreted by fitting a transmission line model (TLM) developed in a previous study to experimental EIS data [31]. The TLM parameter values were assessed in order to gain an understanding of the dominant fouling mechanisms present on the REM as a function of both membrane fouling and regeneration.

2. Materials and Methods

2.1 Reagents. Chemicals were reagent-grade and obtained from Sigma-Aldrich and Bangs Lab (Fishers, IN). All chemicals were used as received. All solutions used in this study were made using purified deionized water obtained from a NANOPure water purification system (Barnstead) with resistivity greater than $18.2 \text{ M}\Omega \cdot \text{cm}$ (25°C), referred to as DI water.

2.2 Reactive Electrochemical Membrane. The REM used in this study was synthesized from an asymmetric TiO_2 UF tubular membrane with a molecular weight cut-off (MWCO) of 50 kDa (TAMI Industries, Les Laurons, France). The TiO_2 membrane was converted to conductive Magnéli phases ($\text{Ti}_n\text{O}_{2n-1}$) in a tube furnace (OTF-1200X, MTI) under a H_2 atmosphere and at a temperature of 1050°C for 30 hours. The outer and inner diameters of the membrane are 10 mm and 5.5 mm, respectively, with a length of 100 mm. The total thickness of the REM is 2.25 mm, the REM active layer thickness is $\sim 60.0 \text{ }\mu\text{m}$ and the support layer thickness is 2.19 mm. The REM was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Hg porosimetry. Porosimetry analysis was performed by Micrometric Analytical Services (Norcross, GA) according to method ISO 15901-

1 [32]. A Hitachi S-3000N SEM was used to investigate the REM morphology and surficial pore size. XRD analysis was conducted on a Siemens D5000 X-ray diffractometer.

Figure 1 (a) System sketch of filtration (fouling) experiment, EIS measurement setup and (b) setup for CFER in backwash mode. Inset image shows a three electrode placement sketch inside the REM. Dead end mode is realized by completely cutting off Line 1 (cross flow) in Setup (a).

2.3 Filtration Setup. Figure 1a shows a schematic representation of the cross-flow UF experimental system combined with a potentiostat to control electrode potential and current. This setup is adapted from our previous work [23]. The feed solution was pumped through the system at a constant cross-flow rate ($Q = 30.6 \text{ L h}^{-1}$), using a bench analog drive gear pump (Cole Parmer) and a trans-membrane pressure of 1.0 bar was maintained using a pressure regulator. In every membrane filtration experiment, the feed was continuously stirred in the feed tank. The permeate flux was measured volumetrically per unit time and normalized by the outer geometric surface area and trans-membrane pressure, which is defined as the membrane permeability (J). Both the retentate and permeate streams were 100% recycled to the feed tank. Each experiment started by recirculating a

100 mM NaClO₄ (pH 5.95) supporting electrolyte through the filtration system at 1.0 bar trans-membrane pressure until a steady-state initial permeate flux was achieved (J_0). An initial EIS measurement was also recorded, which together with J_0 represent the initial conditions of the membrane. The normalized permeate flux $\bar{J}$ is defined as $\frac{J}{J_0}$.

2.4 MWCO Determination. All MWCO experiments on the pristine TiO₂ membrane and REM were performed in the setup shown in Figure 1a in a dead-end filtration mode. Prior to a MWCO experiment, DI water was circulated in the system until steady state J was achieved and permeate flux J_0 was used to indicate the state of the membrane. The feed was replaced with a 0.1 – 2.5 g L⁻¹ dextran standard solution (MW of 6, 10, 20, 40, or 70 kDa), the concentrations of permeate were analyzed using UV-spectroscopy (Shimadzu UV-1800) after a steady state J was reached during the filtration process. The rejection of the dextran solution was calculated based on: $R = (C_f - C_p) / C_p$, where C_p and C_f are the concentrations in permeate and feed solutions, respectively. Details of MWCO experimental methods and results are summarized in *Section 1* of the *Supplementary Information* (SI).

The pore radius of the active filtration layer was estimated from MWCO results and using Equation (5) [33]:

$$r = 0.33 \times (MWCO)^{0.46} \quad (5)$$

where r (Å) is the mean radius of the pore and $MWCO$ (Da) is the molecular weight cutoff.

2.5 Fouling Experiments. Fouling experiments consisted of humic acid and polystyrene microsphere fouling as model natural organic matter (NOM) and particulate foulants, respectively. Synthetic humic acid was chosen as a model NOM foulant because it has a similar structure to NOM found in drinking water sources. It, however, is recognized that this type of humic acid is known to be much larger in size, higher content in aromatic structure, and lower content in acidic functional

groups compared to the commonly used Suwannee river humic acid [34], but was deemed to be appropriate to accomplish the goals of our work (i.e, studying the feasibility of fouling/regeneration at the REM surface). All humic acid solutions were freshly made less than 24 hours prior to each experiment. Humic acid (150 mg L^{-1}) was injected into the feed supporting electrolyte solution and pumped through the membrane in the cross-flow mode with 100% recycle for 120 minutes in order to achieve significant and rapid fouling and compact the fouling layer under the trans-membrane pressure. The open circuit potential (OCP) monitored during this step was 0.37 V vs. the standard hydrogen electrode (SHE). Prior to the regeneration step, 2 L of DI water was pumped through the fouled membrane in order to remove loosely sorbed organic compounds, which is termed as the “DI Water Rinse” step. The reproducibility of humic acid fouling on the REM was examined in different regeneration experiments and during a *Multi-Cycle Test* (Section 3.2.3).

Polystyrene microsphere solutions, 1L of 0.001 wt% polystyrene microsphere (Bangs Laboratory) with a mean diameter of $1.58 \text{ }\mu\text{m}$, were made the same day of the experiment in a 10 mM NaClO_4 supporting electrolyte in order to provide ionic strength similar to natural water conditions. The polystyrene microsphere fouling experiments were performed in dead end inside-out filtration mode, with 100% recycle for 90 minutes. The concentration of $1.58 \text{ }\mu\text{m}$ polystyrene microspheres in the feed and permeate solutions were monitored by UV-Vis spectroscopy at a wavelength of 312 nm. The reproducibility of the polystyrene microsphere fouling on REM was assessed through the comparison of duplicate fouling experiments before different regeneration experiments.

2.6 Chemical Free Electrochemical Regeneration (CFER) Experiments. Membrane regeneration consisted of CFER in either forward wash or backwash mode at $25 \text{ }^\circ\text{C}$. Constant current was applied to both regeneration modes by a direct current power supply (Protek P6035). The electrochemical regeneration in forward wash mode was conducted in the same setup as used in

fouling experiments (Figure 1a), with the REM as the anode and a stainless steel rod with a diameter of 1.52 mm arranged in the center of the REM as the cathode. The anode and cathode were 1.95 mm apart. The electric conductivity measurement was made using an EIS method discussed by Guo et al. [30], and the conductivity of the REM was $15.06 \pm 2.11 \text{ S cm}^{-1}$. Electrical contact to the REM was made using a titanium wire wrapped around the outer diameter of the membrane. The concentric placement of the electrodes insures a uniform potential on the REM surface with respect to REM length and curvature. The 100 mM NaClO_4 supporting electrolyte was pumped through the membrane in the cross-flow mode with 100% recycle for 180 min.

The CFER in backwash mode was conducted as shown in Figure 1b. The backwash suction was achieved by applying 40 mbar vacuum using a vacuum pump (KNF Laboport). The CFER was accomplished using the REM as either the anode or cathode and the stainless steel rod as the counter electrode. The electrode placement is the same as discussed above. Constant current was applied to the cell using a direct current power supply during the filtration of a 1 L 100 mM NaClO_4 electrolyte. For polystyrene microsphere fouled membranes the concentration of microspheres in the regenerant solution was determined by UV spectroscopy. The reproducibility of the regeneration of the humic acid fouled REM was examined during the *Multi-Cycle Test* (Section 3.2.3) and that of the polystyrene microsphere fouled REM was performed in duplicate and results are shown in Section 2 of the *SI*.

The backwash control experiments were performed twice in the setup shown in Figure 1b without an applied current. The first backwash control experiment used 1 L of DI water (30 minutes) accounting for the solution volume effect brought upon by 1 L NaClO_4 electrolyte pumped through the membrane during anodic regeneration in backwash mode. The second backwash control experiment consisted of pumping DI water continuously through the membrane for 1 hour

accounting for the total time spent in pumping 1 L NaClO_4 electrolyte during anodic regeneration in backwash mode.

2.7 Electrochemical Impedance Spectroscopy Measurements and Transmission Line Model

Fitting. Potentiostatic EIS measurements were conducted on the REM shown in Figure 1a using a three-electrode setup, with REM as working electrode, stainless steel rod as counter electrode, and silver wire (diameter = 0.50 mm) as quasi-reference electrode (QRE). Potentials and currents were controlled and measured using a Gamry Potentiostat (Interface 1000). The electrode placement was the same as described above and the QRE was located 1.0 mm from the REM surface. Before each EIS measurement, the QRE was polished to remove the passivation layer and calibrated against a saturated Ag/AgCl reference electrode (1.0 mm from the REM surface). The QRE was used for EIS measurements because the Ag/AgCl reference electrode had high impedance, which interfered with the measurements. EIS measurements were made at the OCP in an electrolyte solution containing 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ with an amplitude of 4 mV in the sinusoid perturbation and over a frequency range of 30 kHz to 10 mHz.

The presence of the redox active species is not expected to have a large effect on the impedance elements. However, there is a possibility of adsorption of the redox active species to the REM surface, which would affect the impedance measurements by changing the interfacial polarization processes. Due to this concern, the EIS measurements were conducted over a short time-scale (*i.e.*, ~15 min) and the REM was thoroughly rinsed afterwards to minimize adsorption of the redox active species. The concentrations of the redox active species were found the same in both the feed and permeate during the filtration process with and without the alternating potential, as shown in *SI* (Figure S-6), and thus indicates a discernable concentration gradient of the redox active species did not exist.

Lissajous curves were also monitored as a real-time assessment of the quality of impedance measurements and thus to ensure good performance of the QRE. The EIS data were also examined by Kramers-Kronig relations to insure the validity of the data and confirm that the measurements were not corrupted by instrument artifacts or transient behavior [35]. The EIS data were fit by a TLM developed by our research group [31]. The TLM decouples the impedances from different layers of the UF REM, and thus has the ability to spatially characterize membrane fouling. The fitting of the TLM to EIS data is realized by a minimization of the sum of the square of the residuals, the model results are also reported along with error estimates calculated at the 95% confidence interval. The double layer capacitance (C_{dl}) and electro-active surface area ($A_{electro}$) of the UF REM can be determined by EIS and calculated through Equation (6) and (7), respectively.

$$C_{dl,m} = \left(\frac{Y_{0,m}}{[R_s^{-1} + R_{ct,m}^{-1}]^{1-\alpha}} \right)^{1/\alpha} \quad (6)$$

$$A_{electro,m} = \frac{C_{dl,m}}{\bar{C}_{dl}} \quad (7)$$

where $Y_{0,m}$ ($F \cdot s^{\alpha-1}$) is the capacitance constant at interface m , α is the exponential factor, $R_{ct,m}$ (ohm) is the charge transfer resistance of interface m , R_s (ohm) is the solution resistance, $\bar{C}_{dl}$ ($\mu F \cdot cm^{-2}$) is the surface normalized double layer capacitance ($m = outer, active or sup$).

Fitted parameters including $R_{ct,m}$, $Y_{0,m}$, α and ionic resistance χ_I , are reported here for the analysis, while the other parameters are tabulated in *Section 4* of *SI*. Details of EIS spectra fit and error estimate calculations are presented in *Section 5* of the *SI*.

Analysis of the penetration depth (λ) of the alternating voltage signal during EIS measurements on an asymmetric UF REM of identical geometry allow for defining characteristic frequency ranges for each representative surface of the REM: high frequencies of 1 to 30 kHz ($\lambda = 0.53 - 2.88 \mu m$) accounts for the outer surface, mid frequencies of 2 Hz to 1 kHz ($\lambda = 2.88 - 64.4 \mu m$) accounts for the

active layer, and frequencies < 2 Hz accounts for the support layer [31]. It is noted that overlapping of outer surface and active layer may exist, since the surface roughness and the boundary between these two layers are not well defined. All experiments, including filtration, fouling, CFER and EIS measurement, were carried out at room temperature (25 °C).

3. Results and Discussion

3.1 Physical Characterization. The dual pore structure of the UF REM is shown in SEM images presented in Figure 2a - c. The thickness of the active layer is ~ 60 μm (Figure 2a). The support layer has a pore diameter that is much larger than the active layer and makes up the remainder of the membrane. Both active and support layers were converted to substoichiometric TiO_2 Magnéli phases, as determined by XRD (Figure 2d). The characteristic peaks for Ti_4O_7 and Ti_6O_{11} are located at 2 theta angles of 20.78° and 22.84° , respectively [29]. The existence of peaks at these two positions indicates that the REM consists primarily of Ti_4O_7 and Ti_6O_{11} . Peaks characteristic of TiO_2 were not present, which indicates a full conversion from TiO_2 to the Magnéli phases was accomplished.

The MWCO experiments were conducted on the TiO_2 membrane and REM. The MWCO of the TiO_2 membrane was 50 kDa and increased to 60 kDa for the REM, which was a result of particle sintering leading to pore size enlargement during the high temperature reduction process (*SI Figure S-1*). Estimates of the pore size according to Equation (5) yielded mean pore diameters of 9.6 and 10.4 nm for the TiO_2 membrane and REM, respectively.

The pore structure of the REM was further characterized by Hg porosimetry, which is shown in Figure 2e and 2f. The REM exhibits a bimodal pore size distribution with surface area of $0.12 \text{ m}^2 \text{ g}^{-1}$ associated with the support layer (pores $> 1.0 \mu\text{m}$) and a surface area of $0.79 \text{ m}^2 \text{ g}^{-1}$ associated with the active layer and the surface roughness of the REM (pores $< 8 \text{ nm}$) (Figure 2e). Nearly the entire pore volume is dominated by the support layer, which contains pores in the range of 1.0 to $3.8 \mu\text{m}$

diameter (Figure 2f). Porosimetry results determined a porosity of 28.2%, specific surface area of $0.94 \text{ m}^2 \text{ g}^{-1}$, and median pore diameter of $3.27 \text{ }\mu\text{m}$ (based on pore volume data), which represents the pore size in the support layer. The total porous surface area of the REM determined by Hg porosimetry was 16.90 m^2 .

Figure 2 SEM of REM, (a) overall SEM image, (b) active layer, (c) support layer; (d) XRD of substoichiometric TiO_2 membrane with red (solid) and green (dash) arrows representing standard characteristic peaks of Ti_4O_7 and Ti_6O_{11} , respectively; results of Hg intrusion porosimetry analysis of (e) cumulative pore area, and (f) log differential intrusion pore volume (solid line represents piece-wise linear interpolation)

The total $A_{electro}$ determined by EIS was $1.9 \pm 0.06 \text{ m}^2$, which indicates that only about 11.4% of the surface area determined by Hg porosimetry was electroactive. The distribution of the electroactive surface area was $4.74 \pm 0.368\%$ outer surface, $18.4 \pm 1.05\%$ active layer, and $78.9 \pm 1.58\%$ support layer. Using the 17.20 cm^2 nominal geometric inside surface area of the REM, the average roughness factor, which is the ratio of electrochemically active surface area to the geometric surface area of the REM, was 1122 ± 34.9 , indicating a high surface area was available for electrochemical reactions.

3.2 Humic Acid Membrane Fouling and Regeneration.

In the following sections, EIS was used to understand REM fouling by humic acid and the CFER scheme was optimized in order to achieve a complete permeate flux recovery. As a model foulant, humic acid is present in most natural waters and is a major foulant during membrane operation [36,37]. Humic acid is usually negatively charged at neutral to high pH due to the deprotonation of the carboxylic and phenolic groups [38], therefore the negatively charged humic acid causes more fouling on a positively charged membrane [39]. Aggregation of humic acid can also occur by a combination of intermolecular hydrophobic interaction involving the aromatic or aliphatic regions of the humic acid, π bonding between aromatic groups, and hydrogen bonding between polar groups [36,40].

3.2.1 Anodic CFER in Forward Wash Mode. Figure 3a shows results for UF of a 150 mg L^{-1} humic acid feed solution, which caused a severe decline in $\bar{J}$ with respect to time ($3.80 \pm 0.71\%$ of initial $1499 \text{ LMH bar}^{-1}$). After the fouling experiment, a DI water rinse increased $\bar{J}$ from 3.80 ± 0.71 to $20.0 \pm 1.1\%$ (Figure 3a). In an attempt to oxidize the adsorbed humic acid from the membrane surface, an anodic CFER of the REM was performed. A constant current of 800 mA (cell potential = 8.2 V; anode potential = 4.9 V) was applied to the electrochemical cell for 180 minutes during inside-out cross-flow operation. Permeate flux was monitored during the CFER (150 to 320 min.) and $\bar{J}$ was $35.0 \pm 0.40\%$ at the end of regeneration (Figure 3a). After which, the permeate flux was again tested (320 to

360 min), and $\bar{J}$ was $37.0 \pm 1.7\%$ (Figure 3a). The CFER in forward wash mode was not able to completely regenerate the humic acid fouled REM, which was hypothesized to be due to an electrode potential drop with depth into the REM pores.

Figure 3 (a) Normalized permeate flux $\bar{J}$ of REM at different operational condition for treatment of 150 mg L^{-1} humic acid feed solution in forward wash mode; initial membrane flux $J_0 = 1499 \text{ LMH bar}^{-1}$; (b1) simulated potential drop along membrane pore and (b2) active layer.

The potential distribution in porous electrodes has been rigorously treated, and an analytical solution has been developed by Lasia [41] (see *SI Section 6*). The calculated potential profile on the REM in a 100 mM NaClO_4 supporting electrolyte is shown in Figure 3b. Results indicate that the potential drops drastically with depth into the porous membrane and the depth at which the potential is able to drive $\text{OH}^\bullet$ production is only approximately $0.023 \text{ }\mu\text{m}$. This calculation is dependent on several parameters (e.g., pore radius, exchange current density, specific solution resistance, and overpotential) and therefore should be taken as a first-order approximation. Nevertheless, this approximation indicates that the majority of the interior porosity of the REM would have a potential much lower than that needed for $\text{OH}^\bullet$ production, and is likely the reason that anodic CFER in forward wash mode did

not fully regenerate the REM. Humic acid has been shown to react readily with $\text{OH}^\bullet$ ($k = 2.28 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [42]), and thus during anodic CFER polyphenolic compounds are likely removed from the outer membrane surface. However, due to potential drop with distance within the membrane only direct electron transfer reactions can occur that prevent efficient ring cleavage and removal of the adsorbed humic acid/phenolic intermediates present within the active layer and membrane support regions. This mechanism would explain the lack of complete flux recovery in the forward wash mode.

Figure 4 (a) Normalized permeate flux $\bar{J}$ under different operational conditions for the anodic CFER in forward wash mode of 150 mg L^{-1} HA fouled REM; (b) EIS spectra in complete frequency range; (c) zoomed-in EIS spectra in high and mid frequency range ; and (d) Bode phase plot; initial membrane flux $J_0 = 1499.0 \text{ LMH bar}^{-1}$. (Solid lines represent TLM fit, unfilled symbols represent characteristic frequency at 10 mHz, 1.0 Hz and 30 kHz and layers of the REM are differentiated through various shades.)

EIS was used to characterize the REM under conditions of fouling and regeneration. It is noted that, in Figure 4d, the characteristic frequency differentiating the active and support layer boundary shifts to a lower frequency from the theoretical determined 2 Hz, which can be explained by the choice of the $\bar{C}_{dl}$ (60 $\mu\text{F}\cdot\text{cm}^{-2}$ in the theoretical calculation) and the variation of specific solution resistance ρ in the sub-micron pore. The value of λ is dependent on $\bar{C}_{dl}$ and ρ [31]. The range of typical $\bar{C}_{dl}$ is commonly on the order of 10-100 $\mu\text{F}\cdot\text{cm}^{-2}$ [43]. The value of ρ increases to 0.089 $\Omega\cdot\text{m}$ from 0.080 due to the decrease of dielectric constant from 80 in the bulk solution to 71.94 in the pores with 5 nm radius [31]. When $\bar{C}_{dl}$ is taken as 100 $\mu\text{F}\cdot\text{cm}^{-2}$, ρ as 0.089 $\Omega\cdot\text{m}$ and λ is kept constant (64.4 μm), the characteristic frequency at the active and support layer boundary decreases to 1 Hz. In Figure 4d, the mesh marks the range of characteristic frequencies that describe the boundary between the active and support layers (1 to 2 Hz). The characteristic frequency of 1 Hz matches the observed time constants in Figure 4d and thus will be used in the analysis henceforth.

The permeate flux change is summarized in Figure 4a, and EIS data and model fits are provided as Nyquist (Figure 4b and 4c) and Bode phase plots (Figure 4d). The parameters of the best-fit TLM to the EIS spectra are provided in Table 1. The adsorption of humic acid leads to a decrease in pore size, and pore constriction at the active layer will increase χ_I , as shown in Table 1, due to the decrease in dielectric constant [31]. Additionally, humic acid fouling leads to an increase in R_{ct} (22-fold increase at the outer surface, 224-fold increase at the active layer, and 7-fold increase at support layer compared to the background), indicating that the adsorption of humic acid decreases the rate of charge transfer. The R_{ct} decrease at both the outer surface (1.3-fold of background) and active layer (5.5-fold of background) after anodic CFER in forward wash mode, suggests partial removal of adsorbed humic acid at these two areas. However, $R_{ct,sup}$ further increases (2.6-fold), indicating the support layer experienced additional fouling during the regeneration process. This interpretation of membrane fouling and

regeneration is also supported by $A_{electro}$ calculations. Membrane fouling causes a decrease in $A_{electro}$ by ~ 50% at all three areas. The anodic CFER recovered most (~77% of the initial) of the A_{outer} and A_{active} and decreased A_{sup} to 23% of the initial value. The change in $A_{electro}$ does not follow an inverse relationship with $R_{ct,m}$, which is due to the inhomogeneity of the REM surface [31].

The Bode phase plot shows a similar trend as the Nyquist plots, but allows for a clearer visualization of fouling at each layer (Figure 4d). The ϕ at all three areas is shifted to more negative values after fouling, which is consistent with results from a theoretical interpretation of REM fouling using a TLM [31]. The ϕ were restored to near background values after CFER, except at the support (low frequency range) (Figure 4d).

It is concluded from the interpretation of the EIS data by the TLM that humic acid fouling takes place at all three representative areas (outer surface, active layer, and support layer), and after anodic CFER the partial regeneration of active layer pores and the outer membrane surface were achieved. However, after regeneration the EIS data suggests further fouling of the support layer, likely due to the polymerization of organic fragments removed from the active layer and flushed into the support during anodic CFER. The low pH generated by reaction (1) likely does not promote humic acid desorption because prior studies suggest that humic acid adsorption is enhanced on TiO_2 at acidic pH [44].

Sodium hydroxide has been shown to promote the dissolution of weakly acidic organic matter with carboxylate functional groups [45], and therefore is used to clean the REM. Therefore, the membrane was soaked in 2.5 wt% sodium hydroxide for 10 hours at room temperature to achieve complete recovery of permeate flux, as shown in Figure 4a, termed as “chemical cleaning”.

3.2.2 Anodic CFER in Backwash Mode.

Analysis showed that only a fraction of the active layer is active for $OH^\bullet$ production. Therefore, it is hypothesized that conducting anodic CFER in the backwash mode would be more efficient because:

(1) desorbed foulants and intermediates during the regeneration process will be physically transported in the direction of higher electrode potential where $\text{OH}^\bullet$ production exists, (2) the dissociation of foulants from the interfaces due to the shear force by the backwash flow, and (3) the enhanced shear force by electrochemically generated gas bubbles and bubble collapse with a release of energy [20,46,47]. While cathodic regeneration would generate basic conditions and should help to desorb humic acid, preliminary results show that it was not effective (data not shown).

Figure 5a shows that $\bar{J}$ decreased to $5.00 \pm 0.30\%$ after the humic acid fouling step, and increased to approximately $34.0 \pm 2.3\%$ after the DI water rinse. Application of the anodic CFER in backwash mode was able to completely recover the membrane flux ($\bar{J} = 118 \pm 8.1\%$). The EIS spectra shown in Figures 5b and 5c and fitted TLM parameter values in Table 2 show a similar response to fouling than those presented in Figures 4b and 4c and Table 1, confirming the reproducibility of the fouling mechanism by humic acid on this REM. After regeneration, both the R_{ct} and $A_{electro}$ at the outer surface and support layer are restored approximately to their background values (Table 2), and the value of χ_l is also brought back to its background value, indicating a restoration of the pore size at the active layer. The recovery of both the active and support layers is directed responsible for the $> 100\%$ recovery of $\bar{J}$. The $R_{ct,active}$ and A_{active} were not fully recovered after CFER in backwash mode, but was not a factor in affecting permeate flux, indicating that some residual monolayer fouling may have persisted in this area.

Figure 5 (a) Normalized permeate flux $\bar{J}$ under different operational conditions for the anodic CFER in backwash mode of 150 mg L^{-1} HA fouled REM; (b) EIS spectra in complete frequency range; (c) zoomed-in EIS spectra in high and mid frequency range; (d) Bode phase plot; initial membrane flux $J_0 = 1592 \text{ LMH bar}^{-1}$. (Solid lines represent TLM fit, unfilled symbols represent characteristic frequency at 10 mHz, 1.0 Hz and 30 kHz and layers of the REM are differentiated through various shades.)

Table 1 Model parameters, calculated double layer capacitances and electro-active surface areas of background, 150 mg L⁻¹¹ HA fouling and anodic CFER in forward flush mode (Unit: χ_l (Ohm), R (Ohm), Y (F·s ^{$\alpha-1$}), C_{dl} (Farad), A (cm²))

Parameter		Background	Error ($\pm$)	HA Fouled	Error ($\pm$)	Anodic CFER	Error ($\pm$)
χ_l		4.30×10^0	2.27×10^{-2}	6.23×10^0	1.88×10^{-2}	4.50×10^0	1.32×10^{-2}
Outer Surface	R _{ct,out}	4.52×10^0	3.65×10^{-1}	1.01×10^2	1.20×10^1	5.89×10^0	1.67×10^{-1}
	Y _{0,out}	1.00×10^{-1}	1.13×10^{-3}	3.04×10^{-2}	6.22×10^{-4}	8.02×10^{-2}	1.14×10^{-3}
	α	7.00×10^{-1}	2.31×10^{-2}	9.23×10^{-1}	5.33×10^{-3}	7.00×10^{-1}	8.34×10^{-4}
Active Layer	R _{ct,active}	4.45×10^0	6.66×10^{-1}	1.00×10^3	9.21×10^1	2.45×10^1	2.16×10^0
	Y _{0,active}	1.16×10^{-1}	5.70×10^{-3}	8.70×10^{-2}	1.82×10^{-3}	1.01×10^{-1}	6.70×10^{-3}
	α	9.60×10^{-1}	6.98×10^{-3}	7.13×10^{-1}	5.89×10^{-3}	8.55×10^{-1}	5.19×10^{-3}
Support Layer	R _{ct,sup}	3.16×10^1	2.09×10^0	2.21×10^2	4.36×10^1	5.68×10^2	8.20×10^1
	Y _{0,sup}	7.00×10^{-1}	5.94×10^{-2}	3.01×10^{-1}	4.52×10^{-2}	1.70×10^{-1}	2.88×10^{-3}
	α	1.00×10^0	2.68×10^{-2}	1.00×10^0	4.64×10^{-2}	8.49×10^{-1}	2.86×10^{-3}
Location		Background	Error ($\pm$)	HA Fouled	Error ($\pm$)	Anodic CFER	Error ($\pm$)
Outer Surface	C _{dl,out}	5.23×10^{-2}	5.45×10^{-3}	2.64×10^{-2}	9.10×10^{-4}	4.06×10^{-2}	1.13×10^{-3}
	A _{out}	8.72×10^2	9.08×10^1	4.40×10^2	1.52×10^1	6.77×10^2	1.88×10^1
Active Layer	C _{dl,active}	1.09×10^{-1}	6.91×10^{-3}	6.77×10^{-2}	2.30×10^{-3}	8.56×10^{-2}	7.33×10^{-3}
	A _{active}	1.83×10^3	1.15×10^2	1.12×10^3	3.83×10^1	1.43×10^3	1.22×10^2
Support Layer	C _{dl,sup}	7.00×10^{-1}	7.43×10^{-2}	3.01×10^{-1}	4.60×10^{-2}	1.60×10^{-1}	3.26×10^{-3}
	A _{sup}	1.17×10^4	1.24×10^3	5.02×10^3	7.67×10^2	2.67×10^3	5.43×10^1

The Bode phase plot shows a shift of φ to more negative values in the high and mid frequency ranges after fouling, and a return to background φ values after the CFER (Figure 5d). The φ values in the low frequency range (support layer) do not change significantly due to fouling, but a significant shift to less negative values is observed after the anodic CFER treatment. The φ values at high frequencies after CFER in backwash mode (Figure 5d) are more comparable to background values shown in Figure 4d, suggesting a more thorough cleaning of the REM than by NaOH chemical cleaning.

Although the anodic CFER in backwash mode is able to fully regenerate $\bar{J}$ of the fouled membrane, it is unclear whether regeneration is due to anodic CFER or the shear force of the backwash itself. Therefore, a control experiment was conducted where the fouled membrane was backwashed twice in the absence of an applied potential. Figure 6a shows $\bar{J}$ was recovered to $57.0 \pm 1.7\%$ after the 1st backwash and $66.0 \pm 2.8\%$ after the 2nd backwash, which suggests that backwash alone cannot fully recover the fouled membrane.

The EIS spectra after the 2nd backwash (Figures 6b and 6c) and best-fit TLM parameter values (Table 3) show that only the active layer experiences a decrease in R_{ct} and increase in A_{electro} . The value of χ_1 , however, is only partially restored to the background value, indicating that backwash cleaning alone is not able to fully remove pore constriction at the active layer [31], compared to a full recovery of χ_1 after CFER in backwash mode, which justifies the effectiveness of this regeneration scheme. The outer surface experiences a significant increase in R_{ct} by 1.6-fold after the backwash, due to adsorption of foulants removed from the active layer and support. An increase in $R_{ct,sup}$ was also observed after backwash, which was attributed to a redistribution of the foulant. However, only A_{out} experienced a decrease after backwash (17.7% of the background A_{out}) and A_{sup} remained unchanged. This result is likely due to the fact that a small portion of regeneration is not statistically

significant in the support layer due to the high value for A_{sup} (56.0% of the total). The Bode phase plot shows a similar behavior as prior humic acid fouling (Figure 6d), which is a shift of φ to more negative values at the fouled regions (i.e., support and active layer).

Table 2 Model parameters, calculated double layer capacitances and electro-active surface areas of background, 150 mg L⁻¹ HA fouling and anodic CFER in backwash mode (Unit: χ_l (Ohm), R (Ohm), Y (F·s⁻¹), C_{dl} (Farad), A (cm²))

Parameter		Background	Error (±)	HA Fouled	Error (±)	Anodic CFER w/ Backwash	Error (±)
χ_l		8.74×10^0	1.11×10^{-2}	1.18×10^1	3.02×10^{-1}	8.50×10^0	5.79×10^{-2}
Outer Surface	R _{ct,out}	1.66×10^2	4.38×10^1	2.32×10^3	6.16×10^1	1.23×10^2	5.95×10^0
	Y _{0,out}	5.58×10^{-2}	1.11×10^{-2}	2.96×10^{-2}	1.20×10^{-3}	6.16×10^{-2}	1.20×10^{-3}
	α	1.00×10^0	2.99×10^{-1}	8.36×10^{-1}	1.70×10^{-2}	7.55×10^{-1}	7.61×10^{-2}
Active Layer	R _{ct,active}	1.46×10^0	1.27×10^0	5.06×10^2	2.01×10^1	1.69×10^0	2.85×10^{-1}
	Y _{0,active}	2.33×10^{-1}	7.65×10^{-2}	6.60×10^{-2}	9.71×10^{-3}	9.51×10^{-2}	1.13×10^{-3}
	α	9.22×10^{-1}	5.31×10^{-2}	9.79×10^{-1}	2.84×10^{-2}	9.51×10^{-1}	3.61×10^{-2}
Support Layer	R _{ct,sup}	5.32×10^2	1.17×10^2	2.14×10^4	1.10×10^3	5.58×10^1	5.38×10^0
	Y _{0,sup}	7.57×10^{-1}	3.73×10^{-2}	6.44×10^{-1}	9.15×10^{-3}	8.83×10^{-1}	1.20×10^{-2}
	α	9.98×10^{-1}	2.85×10^{-3}	9.94×10^{-1}	4.57×10^{-3}	9.94×10^{-1}	4.57×10^{-3}
Location		Background	Error (±)	HA Fouled	Error (±)	Anodic CFER w/ Backwash	Error (±)
Outer Surface	C _{dl,out}	5.58×10^{-2}	2.37×10^{-2}	2.40×10^{-2}	1.92×10^{-3}	4.88×10^{-2}	4.39×10^{-3}
	A _{out}	9.31×10^2	3.95×10^2	4.00×10^2	3.20×10^1	8.14×10^2	7.31×10^1
Active Layer	C _{dl,active}	2.10×10^{-1}	1.01×10^{-1}	6.56×10^{-2}	1.15×10^{-2}	8.73×10^{-2}	7.12×10^{-3}
	A _{active}	3.50×10^3	1.69×10^2	1.09×10^3	1.91×10^2	1.45×10^3	1.19×10^2
Support Layer	C _{dl,sup}	7.58×10^{-1}	3.94×10^{-2}	6.48×10^{-1}	1.24×10^{-2}	8.94×10^{-1}	2.05×10^{-2}
	A _{sup}	1.26×10^4	6.56×10^2	1.08×10^4	2.07×10^2	1.49×10^4	3.42×10^2

Figure 6 (a) Normalized permeate flux $\bar{J}$ under different operation conditions for backwash regeneration of 150 mg L^{-1} HA fouled REM; (Backwash conditions: DI water and 40 mbar vacuum); (b) EIS spectra in complete frequency range ; (c) zoomed-in EIS spectra in high and low frequency range; (d) Bode phase plot; initial membrane flux $J_0 = 1405.0 \text{ LMH bar}^{-1}$. (Solid lines represent TLM fit, unfilled symbols represent characteristic frequency at 10 mHz, 1.0 Hz, and 30 kHz and layers of the REM are differentiated through various shades.)

Table 3 Model parameters, calculated double layer capacitances and electro-active surface areas of background, 150 mg L⁻¹ HA fouling and The 2nd backwash operation (Unit: χ_l (Ohm), R (Ohm), Y (F·s ^{$\alpha-1$}), C_{dl} (Farad), A (cm²))

Parameter		Background	Error (±)	HA Fouled	Error (±)	2 nd Backwash	Error (±)
χ_l		8.28×10^0	2.51×10^{-2}	1.01×10^1	9.88×10^{-2}	9.50×10^0	3.26×10^{-2}
Outer Surface	R _{ct,out}	7.68×10^1	4.92×10^0	8.00×10^1	3.15×10^0	1.22×10^2	5.63×10^0
	Y _{0,out}	4.05×10^{-2}	2.59×10^{-3}	4.04×10^{-2}	1.99×10^{-3}	4.86×10^{-3}	9.26×10^{-5}
	α	7.55×10^{-1}	5.38×10^{-2}	7.93×10^{-1}	2.01×10^{-2}	1.00×10^0	2.26×10^{-2}
Active Layer	R _{ct,active}	7.51×10^0	5.80×10^{-1}	2.43×10^2	1.90×10^1	3.00×10^0	1.39×10^{-1}
	Y _{0,active}	8.17×10^{-2}	4.86×10^{-3}	4.00×10^{-2}	9.22×10^{-4}	8.57×10^{-2}	2.04×10^{-3}
	α	9.05×10^{-1}	2.90×10^{-2}	8.71×10^{-1}	2.26×10^{-2}	8.31×10^{-1}	5.70×10^{-3}
Support Layer	R _{ct,sup}	8.16×10^1	3.54×10^0	1.05×10^3	1.78×10^2	2.00×10^3	3.72×10^2
	Y _{0,sup}	4.01×10^{-1}	1.13×10^{-3}	3.17×10^{-1}	5.22×10^{-3}	2.60×10^{-1}	1.18×10^{-2}
	α	1.00×10^0	3.64×10^{-3}	9.31×10^{-1}	6.25×10^{-3}	8.22×10^{-1}	1.86×10^{-2}
Location		Background	Error (±)	HA Fouled	Error (±)	2 nd Backwash	Error (±)
Outer Surface	C _{dl,out}	2.76×10^{-2}	5.46×10^{-3}	2.76×10^{-2}	3.03×10^{-3}	4.85×10^{-3}	4.15×10^{-4}
	A _{out}	4.59×10^2	9.10×10^1	4.59×10^2	5.04×10^1	8.09×10^1	6.92×10^0
Active Layer	C _{dl,active}	7.35×10^{-2}	7.54×10^{-3}	3.48×10^{-2}	2.09×10^{-3}	6.15×10^{-2}	2.96×10^{-3}
	A _{active}	1.22×10^3	1.26×10^2	5.79×10^2	3.48×10^1	1.03×10^3	4.93×10^1
Support Layer	C _{dl,sup}	4.01×10^{-1}	2.68×10^{-3}	3.48×10^{-1}	7.14×10^{-3}	3.33×10^{-1}	2.78×10^{-2}
	A _{sup}	6.68×10^3	4.46×10^1	5.54×10^3	1.19×10^2	5.54×10^3	4.63×10^2

3.2.3 Multi-Cycle Test

Figure 7 Normalized permeate flux $\bar{J}$ under different operational conditions for the anodic CFER in backwash mode of 150mg L^{-1} HA fouled REM in long term experiment; BG: background, F: fouling, R: anodic CFER; initial membrane flux $J_0 = 1480\text{ LMH bar}^{-1}$; Duration of anodic CFER in backwash mode: 0.5 hour

The effectiveness of the anodic CFER in backwash mode was assessed using a multi-cycle fouling and regeneration experiment. A combination of humic acid fouling and the anodic CFER in backwash mode was conducted for 5 continuous cycles of fouling and regeneration (i.e., the regenerated membrane in one cycle would be directly fouled in the following cycle). Figure 7 shows values for $\bar{J}$ under different operating conditions in the long-term experiment. The $\bar{J}$ during all 5 fouling cycles was $\sim 3.00 \pm 1.0\%$. After the DI rinse step $\bar{J}$ was recovered to between 27.0 ± 1.7 and $37.0 \pm 1.7\%$, and the anodic CFER in backwash mode was able to recover $\bar{J}$ to between 76.0 ± 1.1

and $99.0 \pm 0.57\%$ during the 5 cycles. These results indicate that the anodic CFER in backwash mode can be used as an effective off-line cleaning method for a near complete recovery of $\bar{J}$ after humic acid fouling. EIS spectra collected during the Multi-Cycle Test are presented in *SI Section 7* and results show that the active layer is not fully recovered in cycles 1, 3 and 4, and the values of χ_1 are 1.18, 1.23 and 1.21-fold greater than that of the background, respectively, which indicates residual fouling at the active layer. The permeate recoveries in these three cycles were 76%, 99%, and 93%, suggesting that full active layer regeneration is not needed to obtain full flux recovery, since significant pressure drop takes place across the thick support layer.

3.3 Polystyrene Microspheres Membrane Fouling and Regeneration

Polystyrene microspheres are often used as a model particulate foulant [48] and result in pore blockage and cake layer formation fouling mechanisms. In this study, a 0.001 wt% polystyrene microsphere solution with a mean diameter of 1.58 μm was prepared in 10 mM NaClO_4 supporting electrolyte. In the regeneration experiment, both cathodic CFER in backwash mode and anodic CFER in backwash mode were conducted separately in order to test if electrostatic interactions between the polystyrene microspheres and the REM surface have an effect on regeneration. The zeta potentials (-10.8 – 15.7 mV) of polystyrene microspheres in pH 2.0 to 12 solutions were all negatively charged (*SI Figure S-9*). Therefore, better membrane flux recovery under cathodic CFER was expected, since negatively charged microspheres can be electrostatically repelled from a cathodic polarized membrane surface. In the fouling experiments, 1.58 μm polystyrene microspheres were filtered through the REM, and are completely rejected by the membrane active layer, causing only external membrane fouling. The concentration decay of polystyrene microspheres in the recycled feed solution during the 90-minute filtration experiment is shown in *SI (Figure S-10)*. The

concentrations of polystyrene microspheres in the permeate solutions were below the detection limit (2.0 mg L^{-1}), which indicates substantial rejection.

3.3.1 Polystyrene Microsphere Fouling

The fouling of the REM with $1.58 \text{ }\mu\text{m}$ polystyrene microspheres caused $\bar{J}$ to decrease to between $31.0 \pm 2.5\%$ and $45.0 \pm 3.6\%$ during the three fouling experiments (Figure 8a). It was also observed that the $\bar{J}$ of the fouled membrane was not completely recovered ($62.0 \pm 4.3\%$) by a single backwash treatment. To gain insight into the fouling mechanism, the common filtration law model [49] was fitted to the permeate flux data. The filtration law model has the following form:

$$\frac{d^2t}{dV^2} = \beta \left(\frac{dt}{dV} \right)^\phi \quad (9)$$

where t (min) is the operational time, V (mL) is accumulated permeate volume at time t , β is the blocking law filtration coefficient and the units depend on the value of ϕ (the dimensionless blocking law filtration exponent). Different ϕ values represent different fouling modes. As shown in Figure 8b, ϕ values are 0.89 in the anodic CFER experiment and 0.70 in the cathodic CFER experiment, which are between 0 and 1. The ϕ values suggest that the fouling mechanism is intermediate pore blocking, which assumes the particles reaching the membrane surface obstruct pores and also deposit in multilayers or as a cake layer, or a combination of the two fouling mechanisms [50]. Both the permeate flux data after REM fouling and fouling mechanism extracted from the filtration law confirm the reproducibility of polystyrene microspheres fouling on the REM. Replicate experiments are shown in *Section 2* of the *SI*.

Figure 8 (a) Normalized permeate flux $\bar{J}$ under different operational conditions for regenerations of 0.001 wt% polystyrene fouled REM, initial membrane flux $J_0 = 2286.0$ LMH; (b) filtration law (Equation 9) fit of permeate flux, fit equation: $y = a \cdot x + b$, R^2 after the exponential fit Line 1: 0.995, Line 2: 0.926.

As shown in both Figures 9a and 9c and Table 4, compared to the background EIS spectra, the EIS data after membrane fouling shows an increase of R_{ct} and decrease of $A_{electro}$ at all three representative areas. The rejection of microspheres by the active layer should only cause fouling at the outer surface. The membrane “fouling” observed at the active and support layers is due to the fact that pore blockage by the microspheres restricts access of the redox couple and thus increases values for $R_{ct,active}$ and $R_{ct,sup}$ at these locations. The hypothesis of intermediate pore blockage is supported by the EIS simulations that show the emergence of two distinct semi-circles over the investigated frequency range and also a significant increase of χ_I after fouling [31]. Membrane fouling in the cathodic CFER experiments was greater than that in anodic CFER experiments, which reflects the variability of fouling that is inherent in cake layer fouling. This variability may be due to an uneven pressure drop that develops across the membrane during cake layer formation and back diffusion of the PS. Consequently the fouled membrane in cathodic CFER has much less A_{out} (24-fold decrease) and produces a more distinct semi-circle at mid frequencies (Figure 9a and 9b), which resembles the EIS simulation results of intermediate pore blockage [31]. The experimental Bode phase plots are

also consistent with TLM simulations [31]. Figure 9b and 9d show that the φ at the high frequency range shifts to more negative values and at the low frequency range shifts to less negative values.

Figure 9 EIS spectra (a) and Bode phase plot (b) in cathodic CFER of polystyrene fouled membrane in backwash mode; EIS spectra (c) and Bode phase plot (d) in anodic CFER of polystyrene fouled membrane in backwash mode. (Solid lines represent TLM fit, unfilled symbols represent characteristic frequency at 10 mHz, 1.0 Hz, and 30 kHz and layers of the REM are differentiated through various shades.)

Table 4 Model parameter and calculated double layer capacitances of background, 1.58 μm polystyrene fouling and cathodic/anodic CFER in backwash mode (Unit: χ_I (Ohm), R (Ohm), Y ($\text{F}\cdot\text{s}^{-1}$), C_{dl} (Farad), A (cm^2)). Results for replicate experiments are included in the SI.

a. Cathodic CFER in Backwash Mode							b. Anodic CFER in Backwash Mode									
Parameter		Background	Error (±)	PS Fouled	Error (±)	Regeneration	Error (±)	Parameter		Background	Error (±)	PS Fouled	Error (±)	Regeneration	Error (±)	
χ_I		7.13×10^0	4.23×10^{-2}	8.19×10^1	2.27×10^{-2}	1.01×10^1	1.83×10^{-2}	χ_I		1.56×10^1	9.38×10^{-2}	5.99×10^1	7.77×10^{-2}	1.99×10^1	3.24×10^{-2}	
Outer Surface	$R_{\text{ct,out}}$	3.89×10^1	2.03×10^0	2.92×10^4	5.03×10^2	3.89×10^1	3.13×10^0	Outer Surface	$R_{\text{ct,out}}$	2.18×10^1	5.08×10^0	1.11×10^2	1.59×10^1	9.74×10^0	4.54×10^{-1}	
	$Y_{0,\text{out}}$	4.03×10^{-2}	1.09×10^{-3}	9.87×10^{-4}	1.64×10^{-5}	1.47×10^{-2}	9.05×10^{-4}		Outer Surface	$Y_{0,\text{out}}$	6.54×10^{-3}	3.46×10^{-4}	1.54×10^{-3}	5.21×10^{-4}	1.29×10^{-2}	5.10×10^{-3}
	α	7.03×10^{-1}	2.46×10^{-2}	1.00×10^0	1.31×10^{-1}	1.00×10^0	7.07×10^{-2}			Outer Surface	α	9.88×10^{-1}	1.30×10^{-2}	1.00×10^0	1.01×10^{-1}	9.09×10^{-1}
Active Layer	$R_{\text{ct,active}}$	4.26×10^0	1.20×10^{-1}	1.85×10^4	3.46×10^2	6.00×10^0	3.85×10^{-1}	Active Layer			$R_{\text{ct,active}}$	7.73×10^0	2.83×10^{-1}	3.64×10^1	5.66×10^0	8.78×10^0
	$Y_{0,\text{active}}$	1.22×10^{-1}	1.04×10^{-2}	9.12×10^{-3}	2.05×10^{-4}	1.11×10^{-1}	1.36×10^{-2}		Active Layer		$Y_{0,\text{active}}$	1.64×10^{-1}	2.92×10^{-2}	2.95×10^{-2}	6.91×10^{-4}	1.63×10^{-1}
	α	9.60×10^{-1}	6.43×10^{-3}	1.00×10^0	8.84×10^{-2}	9.94×10^{-1}	3.01×10^{-2}			Active Layer	α	7.00×10^{-1}	2.21×10^{-2}	9.11×10^{-1}	3.98×10^{-2}	9.21×10^{-1}
Support Layer	$R_{\text{ct,sup}}$	3.67×10^1	2.88×10^0	7.72×10^1	6.47×10^0	8.29×10^1	3.02×10^0	Support Layer			$R_{\text{ct,sup}}$	6.49×10^1	3.46×10^0	4.95×10^2	6.49×10^1	4.81×10^1
	$Y_{0,\text{sup}}$	5.69×10^{-1}	3.95×10^{-3}	2.36×10^{-1}	2.36×10^{-3}	2.01×10^{-1}	1.50×10^{-3}		Support Layer		$Y_{0,\text{sup}}$	2.93×10^{-1}	2.65×10^{-3}	1.94×10^{-1}	1.84×10^{-2}	3.52×10^{-1}
	α	9.32×10^{-1}	1.73×10^{-3}	7.03×10^{-1}	3.33×10^{-3}	9.05×10^{-1}	5.70×10^{-3}			Support Layer	α	9.44×10^{-1}	3.64×10^{-3}	7.55×10^{-1}	3.46×10^{-3}	9.24×10^{-1}
Location		Background	Error (±)	PS Fouled	Error (±)	Regeneration	Error (±)	Location			Background	Error (±)	PS Fouled	Error (±)	Regeneration	Error (±)
Outer Surface	$C_{\text{dl,out}}$	2.65×10^{-2}	2.46×10^{-3}	1.08×10^{-3}	5.87×10^{-4}	1.47×10^{-2}	2.98×10^{-3}	Outer Surface	$C_{\text{dl,out}}$		6.31×10^{-3}	5.96×10^{-4}	1.54×10^{-3}	1.15×10^{-3}	1.03×10^{-2}	5.37×10^{-3}
	A_{out}	4.41×10^2	4.10×10^1	1.81×10^1	9.78×10^0	2.46×10^2	4.96×10^1		Outer Surface	A_{out}	1.05×10^2	9.94×10^0	2.57×10^1	1.92×10^1	1.72×10^2	8.95×10^1
Active Layer	$C_{\text{dl,active}}$	1.18×10^{-1}	1.11×10^{-2}	7.96×10^{-3}	1.57×10^{-3}	1.09×10^{-1}	1.60×10^{-2}	Active Layer		$C_{\text{dl,active}}$	1.48×10^{-1}	4.00×10^{-2}	2.83×10^{-2}	2.22×10^{-3}	1.60×10^{-1}	3.13×10^{-2}
	A_{active}	1.96×10^3	1.86×10^2	1.33×10^2	2.62×10^1	1.82×10^3	2.67×10^2		Active Layer	A_{active}	2.46×10^3	6.67×10^2	4.72×10^2	3.71×10^1	2.67×10^3	5.22×10^2
Support Layer	$C_{\text{dl,sup}}$	6.41×10^{-1}	7.50×10^{-3}	3.44×10^{-1}	8.34×10^{-3}	2.17×10^{-1}	2.92×10^{-3}	Support Layer		$C_{\text{dl,sup}}$	3.12×10^{-1}	4.36×10^{-3}	2.52×10^{-1}	3.14×10^{-2}	3.85×10^{-1}	9.28×10^{-2}
	A_{sup}	1.07×10^4	1.25×10^2	5.74×10^3	1.39×10^2	3.62×10^3	4.86×10^1		Support Layer	A_{sup}	5.21×10^3	7.26×10^1	4.20×10^3	5.23×10^2	6.42×10^3	1.55×10^3

3.3.2 Membrane Regeneration

After the application of either a cathodic or an anodic CFER to the REM in backwash mode, the $\bar{J}$ values were completely recovered (Figure 8a). The flux was not completely restored for the backwash treatment without an applied electrode potential, which showed $\bar{J}$ of $62.0 \pm 4.3\%$ (Figure 8a). These results suggest that electrochemical reactions also had an influence on the regeneration process. In the spent backwash solution, the normalized concentrations of polystyrene microsphere washed out of the REM for anodic and cathodic CFER were 78.0% and 82.0%, respectively.

From the fitted model parameters shown in Table 4, the decrease in R_{ct} over all three interfaces indicates restoration of the membrane and decrease in χ_1 indicates that the pores at the active layer are accessible to the active redox couple after the regeneration. However, the regeneration is only due to the removal of the fouling layer at the outer REM surface, which allows the redox couple to regain access to the active and support layers. These observations also support the calculated $A_{electro}$ values in Table 4, which show near complete recovery. Figure 8a shows that both anodic and cathodic CFER in backwash mode produced a higher permeate flux ($103 \pm 2.4\%$ after cathodic CFER and $118 \pm 7.4\%$ after anodic CFER) than that in backwash only operation ($62 \pm 4\%$). The Bode phase plots show that a shift to less negative ϕ in the high frequencies after the CFER, which justifies the recovery of the outer surface. Although $\bar{J}$ was completely restored after regeneration (Figure 8a), the EIS spectra were not identical to background conditions. This result indicates that either surface passivation or other changes to the REM may have occurred. Further work is needed to investigate the dimensional stability of the REM during fouling and regeneration cycling.

The zeta potential of the microspheres were negatively charged at all pH values, most likely due to residual sulfonate groups leftover during the polystyrene microsphere synthesis process. Since both anodic and cathodic CFER were equally effective, the electrostatic interactions between the microspheres and the REM do not appear to be an important mechanism for regeneration. However, the fact that both anodic and cathodic CFER in backwash mode were able to completely recover the fouled membrane and backwash alone was not, indicates that an electrochemical potential is a necessary step during membrane regeneration. Therefore, the possible reasons for better flux recovery during electrochemical regeneration is likely related to the interaction of electrochemically produced gas bubbles with microspheres. However, the mechanism for regeneration needs further study.

4. Conclusions

A substoichiometric TiO_2 REM was successfully synthesized from a TiO_2 UF tubular membrane and the main composition was Ti_4O_7 and Ti_6O_{11} . Two model foulants, humic acid and polystyrene microspheres, were used for the investigation of REM fouling. An EIS technique was used to spatially characterize membrane fouling. Based on the information obtained from EIS characterization, a new CFER scheme was developed that utilized electrochemical regeneration in backwash mode, and was able to fully recover a fouled membrane without chemical reagent addition. The REM also proved to be durable and stable in a multi-cycle experiment consisting of 5 consecutive fouling/regeneration cycles. The use of a redox active species for EIS measurements does not allow this method to be used for in situ measurements. Future studies should explore using EIS measurements in the oxygen evolution region so that the addition of a redox active species can be avoided. The power consumption during the non-optimized membrane regeneration procedure was low, at only 0.61 kWh m^{-2} (geometric surface

area) for anodic CFER of both humic acid fouled and polystyrene microsphere fouled REMs with backwash (5.36 V average cell potential and 0.70 A current for 30 min) and 0.39 kWh m⁻² for cathodic CFER of polystyrene microsphere fouled REM with backwash (3.43 V average cell potential and 0.70 A current for 30 min). Using an estimated price of electricity of \$0.10 kWh⁻¹, the additional operating cost of applying electrical current to the REM would be between \$0.06 m⁻² and \$0.04 m⁻² per regeneration cycle for anodic and cathodic CFER, respectively. In this study, a 100 mM salt solution was used to provide sufficient ionic strength, and would add additional cost to the process. The cost of refined salt used in the chemical industry is \$150 ton⁻¹, preparing a 100 mM salt solution adds an additional \$0.28 m⁻² per regeneration cycle. Therefore, the use of the onsite water sources should be investigated.

The chemical costs for chemical regeneration in a 2.0 wt% NaOH solution are \$3.86 m⁻² per regeneration cycle without including shipping costs. The cost of NaOH is \$0.27 lb⁻¹ [51], and increases to \$2.72 lb⁻¹ [52] if shipping is considered, indicating chemical cleaning could be as high as \$38.60 m⁻². The advantage of an electrochemical regeneration scheme is the elimination of traditional membrane cleaning using chemical reagents, which is not only cost effective and time efficient, but also environmentally friendly. This study has not addressed CFER performance in a water source of low conductivity nor using EIS as a real time on-line monitoring tool, which are topics for further study. However, results of this study are promising and suggest that our novel REM can function effectively in various water treatment applications.

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Electrochemical Impedance Spectroscopy

Asymmetric Sub-stoichiometric TiO_2 Reactive Electrochemical Membrane

Excellent Permeate Flux Recovery