Anaerobic bioreactor

UF membrane module

NF membrane module

Treating Anaerobic Sequencing Batch Reactor Effluent with Electrically Conducting Ultrafiltration and Nanofiltration Membranes for Fouling Control

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Abstract

The anaerobic treatment of industrial wastewater has attracted a significant amount of interest. However, excessive fouling complicates the treatment of anaerobic reactor effluent with membranes, which limits the application of membranes as a tertiary treatment. Here, we use an anaerobic sequencing batch reactor coupled to electrically conducting ultrafiltration and nanofiltration membranes to treat high-strength industrial wastewater containing high concentrations of benzyl alcohol, a commercial paint stripper. We demonstrate that an anaerobic process can be used successfully to degrade this contaminant. We also show that the application of negative electrical potential to the ultrafiltration membrane surface prevents membrane fouling and allows for higher operational fluxes during the treatment of complex wastewater streams. The application of positive potential to the membrane surface increases membrane fouling, as well as hindering the cleaning and recovery of the nanofiltration membranes. Overall, our experimental results demonstrate the feasibility of using electrically conducting membranes

to prevent membrane fouling during the treatment of anaerobic reactor effluent at high operational fluxes.

Keywords

Anaerobic sequencing batch reactor, electrically conducting membranes, ultrafiltration, nanofiltration

1. Introduction

Anaerobic bioreactors are an attractive treatment option for high-strength wastewater [1]. Several advantages associated with anaerobic processes include the generation of methane gas that can be harvested for energy production, reduced sludge production, and no aeration requirements, which reduces process energy demands [2-4]. Anaerobic bioreactors have been demonstrated to be effective at degrading a range of organic contaminants found in industrial wastewater, including benzyl alcohol, a chemical used as a paint stripper [5, 6]. The use of benzyl alcohol in industrial activities, such as airplane depainting, produces large intermittent flows of high organic strength wastewater. Frequently, the flowrate of industrial wastewater depends on the schedule and activity of the industry in question, i.e. flowrates can go to zero on weekends and holidays, unless large flow equalization tanks are used. The option of idling the reactor during low flowrate conditions, as well as their ability to treat high intermittent concentrations, make anaerobic sequencing batch reactors (aSBRs) an attractive option for industrial wastewater treatment when nutrient removal is not a critical issue.

Membranes as a tertiary wastewater treatment technology have been widely applied in areas such as wastewater reuse, desalination pretreatment, and in membrane bioreactors [7]. As a physical separation barrier, ultrafiltration (UF) membranes can effectively retain particulate matter and microorganisms resulting in high quality permeate suitable for further treatment by nanofiltration (NF) [8]. Importantly, membrane modules can be coupled directly to a conventional wastewater treatment processes, and can be easily integrated into existing wastewater treatment trains. Thus, using UF and NF membranes to treat the effluent from aSBR offers the potential of producing extremely high quality water that can be safely discharged or reused.

The water quality of a treatment train incorporating membrane treatment can be tailored by the choice of membranes used in the process. For pressure-driven membranes, better separation and higher quality effluent is typically achieved by using denser membranes that require higher operating pressures, such as NF and reverse osmosis (RO). Typically, feed water to NF and RO membranes requires pretreatment to remove foulants; this pretreatment is often done through the use of less restrictive membranes such as microfiltration (MF) and UF [9]. The use of UF and NF membranes in series to treat bioreactor effluent has been demonstrated to produce excellent water quality, with near complete removal of small organic molecules such as pharmaceuticals and endocrine disruptors [10]. A significant advantage of NF processes over RO is that they operate at lower pressures and do not lead to monovalent salt buildup (e.g. NaCl) in the reactor, which can damage the bacteria responsible for the biological process [11].

Fouling prevention is one of the most challenging aspects of tertiary wastewater treatment with membranes [12-14]. During filtration, suspended and dissolved materials in the water deposit on

the membrane surface, which leads to decreased process performance, increased energy demand, and reduced membrane lifetime [15, 16]. In aerobic membrane bioreactors (MBRs) with submerged membranes, vigorous air scouring is used for the dual purpose of providing oxygen to aerobic bacteria and physically cleaning fouled membrane surfaces [17, 18]. However, air scouring is not advisable during anaerobic processes due to the need for low oxygen concentrations. Several strategies have been proposed to mitigate membrane fouling when scouring is not possible, including: scouring with biogas [19], operating at below a so called “critical flux” value (although this does not prevent fouling over the long term) [20], and using electrical fields to repel charged foulants and bacteria from the membrane surface [21-25].

Electrically conducting membranes have been demonstrated to be effective at solving many of the fouling problems associated with membrane processes, as well as endowing membranes with new functionalities. These membranes have been demonstrated to prevent membrane fouling when used as cathodes during the filtration of high concentrations of organic molecules [24]. Electrically conducting NF and RO membranes demonstrated excellent anti-biofouling and anti-scaling properties when an electrical potential was applied to the membrane surface [23, 25, 26]. In addition, electrically charged membranes have been used as electrocatalytic platforms for the purpose of electrochemically transforming various aqueous contaminants [27, 28]. The use of electroactive membranes for fouling prevention during aerobic MBR processes has been previously explored, but to the best of our knowledge, no one has explored the use of electrically active UF and NF membranes in series for the treatment of anaerobic reactor effluent [22]. Additionally, while the effectiveness of electrically charged membranes in preventing fouling has been demonstrated using simple, single component systems, few studies have demonstrated

the use of this class of membranes in the treatment of complex waste streams containing multiple foulants. Importantly, in studies of most membrane treatment systems, permeate water is recirculated to maintain constant organic concentration, or the systems operate in single pass mode, which means both permeate and feed stream are discarded after passing through membrane. Therefore, there is still a need to investigate the fouling behavior of UF and NF membrane systems in series when treating industrial wastewater at higher recovery rates (90%) while returning membrane concentrate back to the reactor for further treatment, a situation more similar to real applications of this technology.

This study demonstrates the use of an aSBR coupled to an electrically conducting UF and NF membrane system for the treatment of high-strength industrial wastewater containing large concentrations of industrial paint stripper. The ultimate goals of this study were: 1) to evaluate the anaerobic degradation of benzyl alcohol using an aSBR; 2) to prevent fouling of the electrically charged UF membrane (used as a cathode) when treating effluent from the aSBR operating at 90% recovery without any chemical cleaning; and, 3) to study the downstream influence of this treated waste stream on the fouling and subsequent cleaning of an electrically conducting NF membrane system.

2. Materials and Methods

2.1 Materials

Carboxylated multiwall carbon nanotubes (CNT-COOH) were purchased from Cheap Tubes (Cheaptubes Inc. Brattleboro, VT). Polysulfone (PSF) UF supports were purchased from Sepro Membranes (Sepro Membranes Inc., Oceanside, CA); the membranes have a reported molecular

weight cut off of 65 kDa. ACS grade trimesoyl chloride (TMC), MgSO_4 , piperazine (PiP), and polyvinyl alcohol (PVA) were purchased from Fisher Scientific. A surrogate wastewater containing dilute commercial paint-stripper (B&B Tritech 9095, kindly provided by the Air Force Civil Engineering Center) was used as the feed solution for the aSBR. B&B Tritech 9095 contains mainly benzyl alcohol and hydrogen peroxide.

2.2 Conductive Membrane Fabrication

Electrically conducting UF membranes were fabricated based on a previously described process [24]. To summarize, 75 ml of 0.01 mg/ml CNT-COOH in DIW were pressure deposited onto the PSF support. Then, a solution of PVA in DIW was pressure deposited onto the support for a final weight ratio of 3:1 PVA to CNTs. The PVA layer was then cross-linked to the membrane support by submerging in a 90°C solution of 1 g/l glutaraldehyde and 0.37 g/L of hydrochloric acid in DIW for 1 hour. Once complete, the UF materials were stored at 4°C.

The fabrication of electrically conducting NF membranes has also been described in a previous paper [23, 26]. Some modifications were made: 50 ml of 0.01 mg/ml CNT-COOH in DIW were pressure deposited onto the PSF support. The support was then soaked in an aqueous PiP (2%) solution for 2 minutes. A rubber roller was used to remove excess water prior to immersing the membrane in a 0.15% TMC solution in hexane. After 1 minute, the membrane was removed from the hexane, dried in an oven at 90°C for 10 minutes and stored at 4°C.

2.3 Membrane and Water Characterization

The electrically conducting UF and NF membranes were characterized using a range of instruments. Images of the membrane surface were obtained using scanning electron microscopy (SEM; FEI XL30 SEM-FEG; Hillsboro, OR) with no sputter-coating. Membrane roughness was measured using atomic force microscopy (AFM; Bruker, Billerica, MA). Contact angle measurements were performed using a contact angle goniometer (Attension, Linthicum Heights, MD). Membrane conductivity was measured using a 4-point conductivity probe (Veeco, Plainview, NY).

Multiple analytical tools were used to characterize the water quality throughout the treatment process. Total organic carbon (TOC; OI Analytical, College Station, TX) and chemical oxygen demand (COD; Hach, Loveland, CO) were used to evaluate aSBR and membrane performance by sampling the feed, effluent and permeate at different treatment stages. Total suspended solids (TSS) were analyzed following Standard Methods procedures [29]. The turbidity of the different water samples was measured using a turbidity meter (Hach, Loveland, CO). Water conductivity was measured using a conductivity probe (Thermo Scientific, Waltham, MA). High pressure liquid chromatography (HPLC; Agilent, Santa Clara, CA) was used to determine the concentration and identities of the different organic compounds in the reactor, reactor effluent, and UF permeate. HPLC calibration curves were prepared for benzyl alcohol and benzoic acid for analysis on an XDB-C-18 column. HPLC operating conditions were: flow rate = 1 ml min⁻¹, injection volume = 100 μ l, detector wavelength = 254nm. The mobile phase was 3:97 of acetonitrile:10mM formic acid at 0 – 4.5 min, 70:30 of acetonitrile:10mM formic acid at 4.5 – 7 min and 3:97 of acetonitrile:10mM formic acid at 7 – 9 min.

2.4 Feed Water Source for aSBR and Membrane

The feed solution for the aSBR was created by diluting B&B Tritech 9095 into dechlorinated tap water to produce a COD of 2000 mg/L. In addition, a commercial fertilizer (Vigoro All Purpose Liquid Plant Food) was added to the reactor (1 g/L) to provide nitrogen and phosphorous to the bacteria. The effluent of the aSBR was fed directly to the UF system, and the UF permeate was used as the feed solution for the NF system.

2.5 Anaerobic Sequencing Batch Reactor and Membrane Treatment Operational Procedures

A water treatment train coupling the aSBR to the UF and NF membrane systems was used in these experiments (Figure 1). When the membrane systems were operated at 90% recovery, the final retentate from the UF and NF systems (10% of the original feed volume) was returned to the aSBR.

Figure 1. System schematic and process diagram for an aSBR coupled to a UF and NF membrane process.

The reactor (3 L) was operated on a 24 hour cycle (Figure 1). At the beginning of each cycle, the reactor was fed 1 L of feed solution and allowed to react for 21 hours. During the reaction phase, the reactor was continuously stirred at a constant 35°C. Any gases produced during the degradation process were allowed to escape the system. After 21 hours, stirring was stopped, and

the reactor was allowed to settle for 3 hours. Following the settling step, 1 L of the reactor content was decanted from the top, analyzed, and used as the feed solution for the UF system. The electrically conducting UF membrane was placed in a custom-built flat sheet membrane module that allows an external electrical potential to be applied to the membrane surface and contains a titanium counter electrode situated 4 mm above the membrane surface (Figure S1). A 3 mm thick polypropylene mesh spacer was placed between the membrane and counter electrode. The effective area of the membrane was 40 cm².

Prior to the start of the experiment, the UF membrane was compressed at 90 psi with DIW for at least 48 hours until the flux stabilized. Flow and pressure to the UF system was provided by a rotary vane pump (McMaster-Carr, Santa Fe, CA), with cross-flow velocity of 20 cm/s. Electrical potentials were applied to the membrane surface and counter electrode by connecting the system to an arbitrary waveform generator operating in DC mode (Rigol, Oakwood Village, OH). The UF system was operated at constant flux unless otherwise specified, which was maintained by adjusting the pressure in the UF membrane module. The optimal electrical potential was determined by comparing the effect of 0 V, 3 V, and 5 V of negative surface potential on membrane fouling using aSBR effluent under constant feed concentrations; under constant feed concentrations, aSBR effluent was introduced to the UF membrane, with both the feed and permeate returning to the feed reservoir (no recovery).

To test the UF membrane's ability to withstand fouling while operating at 90% recovery, we compared membrane performance as a function of applied potential (0 V vs. 5 V as cathode) while not recycling the membrane permeate. In these experiments, the membrane was operated

at a constant flux of 40 LMH, with no backwashing. To test the long-term performance of the UF system at 90% recovery, the UF membrane system was run with the optimal electrical potentials identified previously. Here, three batches of decanted aSBR effluent were run consecutively through the system at 90% recovery with different electrical conditions (-5 V, -5 V/+1.5 V, and 0 V) with no physical or chemical cleaning between each batch. During these experiments, the membrane was backwashed every 30 minutes for 1 minute with permeate.

An Arduino-based control system was used to monitor, maintain and record the operating conditions, including flow rate and velocity, membrane flux, and pressure [24]. Membrane flux was determined by collecting and weighing the membrane permeate. Automatic backwashing was controlled through the Arduino system, and was performed using a peristaltic pump (Cole Parmer, Vernon Hills, IL), which used UF permeate as the backwashing fluid. During backwashing events, different electrical potentials were applied to the membrane surface (0 V, -5 V, and +1.5 V). The UF permeate was characterized in terms of TOC, COD, TSS, turbidity, and conductivity, and used as feed solution for the NF system.

The electrically conducting NF membrane was used in a similar flow module in flat-sheet configuration as described above, except that this module was reinforced with steel plates to withstand the higher pressures used during the NF process. Additionally, the NF module did not contain a mesh spacer (Figure S1). The effective area of the membrane was 40 cm². Prior to the start of the experiments, the NF membranes were compressed at 200 psi for at least 48 hours in DIW until the flux stabilized. Flow and pressure for the NF system were provided by a

diaphragm pump (Wanner Engineering, Minneapolis, MN), with a cross-flow velocity of 20 cm/s.

Feed water for the NF membrane was UF permeate. The NF membrane was tested under three electrical conditions (0 V, -5 V, and +1.5 V); in all cases, the potential was applied as DC, and the membrane was used to recover 90% of the NF feed. All NF experiments were done in duplicate. An Arduino-based control and data acquisition system was used for the NF process, similar to the one described above for the UF system. The electrical potential was applied to the NF membrane by an arbitrary waveform generator, and the system was operated at a constant pressure (180 psi). Membrane cleaning was conducted immediately after the fouling experiments using DI water at a crossflow velocity of 20 cm/s. NF permeate was characterized in terms of TOC, COD, TSS, Turbidity, and conductivity.

3. Results and Discussion

3.1 Membrane Fabrication and Characterization

The electrically conducting UF membranes used in this study have been extensively characterized in a previous study [24, 30]. A summary of the UF membrane characteristics can be seen in Table 1. Briefly, the PVA-CNT-COOH network deposited on the surface of the PS35 PSF support creates a smooth (46 ± 2 nm), electrically conducting (1132 ± 32 Ω /square) robust layer that can be backwashed without experiencing delamination from the PSF support (Figure 2a, c). The CNT-COOH and PVA molecules are covalently bound through ester and ether bonds between the hydroxyl and carboxyl groups on the molecules using glutaraldehyde as the cross-linking agent [24]. Due to the very porous network of CNTs, the rejection properties of the

composite structure are governed by the underlying PS35 PSF support (MWCO = 65 kDa) [24]. The use of the highly hydroxylated PVA molecule in the electrically conducting layer renders the surface very hydrophilic, with a water contact angle of $32 \pm 3^\circ$ (Table 1, Figure S2).

Table 1. UF and NF membrane properties.

Membrane Characterization	UF Membrane	NF Membrane
Root Mean Squared Roughness (nm)	46.37 ± 2.37	13.84 ± 0.99
Resistivity (Ω/sq)	1132 ± 32	1191.3 ± 16.2
Contact Angle ($^\circ$)	32 ± 2.8	37.1 ± 0.08
<u>MgSO₄</u> Rejection	0%	$96 \pm 2\%$
Permeability (LMH/psi)*	34.6 ± 0.77	0.19 ± 0.02

* LMH (Liter $m^{-2} hr^{-1}$).

The electrically conducting NF membranes used in this study are a slightly modified version of the membrane material described previously [23, 26]. The only significant difference was the use of PiP instead of m-phenylenediamine, which modified ion rejection and surface roughness. NF membrane properties are summarized in Table 1. When challenged with MgSO₄ or NaCl solution (1.5 g/L) the NF membranes used in this study exhibited a $96 \pm 2\%$ and $60 \pm 6\%$ rejection, respectively. In these membranes, the polyamide is covalently bound to the surface of the CNTs through ester bonds formed between the TMC molecule and hydroxyl groups on the CNTs [23, 26]. SEM images of the membrane surface can be seen in Fig. 2b; AFM image analysis of the NF membrane surface yielded a surface roughness of 14 ± 1 nm, which is similar to the roughness of commercially available NF membrane materials (Figure 2d) [31, 32]. SEM images of the membrane surface reveal a structure that is similar in appearance to commercially available NF

membranes made with PiP (Figure 2b) [33]. The electrical resistivity of the NF membrane was determined to be $1,191 \Omega/\text{square}$, and the contact angle was found to be $37 \pm 0.1^\circ$ (Figure S2).

Figure 2. SEM images of (a) UF membrane surface, and (b) NF membrane surface. AFM images of (c) UF membrane surface, and (d) NF membrane surface. AFM images were used to calculate the surface roughness of the membranes.

3.2 Anaerobic Reactor Performance and Reactor Effluent Quality

The decanted effluent characteristics (COD removal, TSS, and turbidity) from the aSBR are plotted over time in Figure 3a. It took approximately 6 months for the reactors to achieve stable operating conditions. However, once these conditions were achieved, the reactor maintained excellent COD removal capacity, with COD removal ranging between 80-90% after 24 hours (Figure 3a). TSS and turbidity levels in the decanted water showed some variability that was attributed to the handling of the decanting process, with TSS values generally maintained below 65 mg/L and turbidity below 80 NTUs. However, most days had values that were significantly below these values (Figure 3a). Reactor effluent used during the membrane experiments was taken during days when the turbidity was below 20 NTUs. The reactor effluent contained

278 16.2±2.4 ppm of TSS and 13.7±1.8 ppm of VSS, with a ratio of 0.86 VSS/TSS (Table 2). VSS in
 279 wastewater is typically associated with the presence of bacteria, microbial degradation products,
 280 and other cellular products, such as extracellular polymeric substances [34]. Thus, the majority
 281 of TSS in the decanted reactor effluent is organic on nature. An SEM image of a fouled UF
 282 membrane demonstrates the complex nature of the decanted reactor effluent; the SEM image
 283 shows multiple bacteria and an abundance of amorphous organic matter covering the membrane
 284 surface, demonstrating the complex nature of the membrane feed stream (Figure 3b). HPLC
 285 analysis of water taken at different time points from the reactor shows the changes associated
 286 with the microbial transformation of the organic content of the reactor feed (Figure 3c). Here, the
 287 original organic compound (benzyl alcohol, $t=3.63$ min) is rapidly transformed to benzoic acid
 288 ($t=4.06$ min). A minor component of the feed (benzaldehyde, $t=4.53$ min) is not detected in the
 289 reactor effluent. Another small peak, detected at 0.56 min, grows with time; we were unable to
 290 identify this peak, but speculate it is a small organic acid due to its short elution time.

Figure 3. (a) aSBR performance in terms of COD removal, TSS and turbidity of decanted effluent. Data is presented from day 180 onward; prior to this time, reactor performance was highly variable, and the data is not displayed. (b) SEM image of fouled UF membrane, which was used to filter anaerobic reactor effluent. Red circles indicate bacteria; inset: bare (clean) PVA-CNT UF membrane (c) HPLC analysis at different experimental points with identifiable peaks. The black line corresponds to the reactor feed, the red line corresponds to the reactor contents after 5 hours of operations, and the blue line corresponds to the decanted reactor effluent. Peak identities were confirmed by injecting pure standards.

HPLC analysis of the aSBR content after 5 hours of reaction, as well as the decanted effluent, demonstrate the temporal changes in the concentration and speciation of the organic molecules in the reactor (Figure 4). The main intermediate transformation product of benzyl alcohol was identified as benzoic acid, which is in agreement with previously reported work on the anaerobic degradation pathways of benzyl alcohol [5, 6]. Furthermore, it has been reported that during the anaerobic degradation of benzyl alcohol, benzoic acid forms and then disappears, with methane and very small concentrations of volatile fatty acids as the final degradation products [6]. In the aSBR, the concentration of benzyl alcohol rapidly drops over the reaction time, with the primary degradation product, benzoic acid, emerging and then declining as the bacteria in the reactor continue the degradation process (Figure 4). After 5 hours, the concentration of benzyl alcohol in the aSBR drops by 84%, and after 21 hours of reaction, we could not detect any benzyl alcohol in the reactor (Figure 4). The concentration of the main transformation product, benzoic acid, rapidly increases to a concentration of 284 ppm after 5 hours, and then declines to zero in the aSBR effluent (after 21 hour). As mentioned before, the overall COD removal stabilized at approximately 86% in the aSBR (Figure 3a).

315

316

317 **Figure 4.** HPLC analysis of benzyl alcohol and benzoic acid concentrations measured at
 318 different experimental points. HPLC measurements were done in triplicate with error bars
 319 representing 95% confidence intervals.

320 **3.3 UF Membrane Performance - Determining Optimal Operating Conditions**

321 The decanted effluent from the aSBR was used as the feed for the UF membrane system. Since
 322 the main degradation products of the anaerobic processes (other than methane, hydrogen and
 323 carbon dioxide) have been identified as negatively charged small molecules, it was expected that
 324 the application of a negative potential to the membrane surface would reduce the extent of
 325 membrane fouling during the treatment of the aSBR effluent [35-37]. The application of a
 326 negative potential to the surface of the electrically conducting UF membranes had a significant
 327 impact on membrane fouling during the filtration of aSBR effluent (Figure 5a); here, the system
 328 was operated at a constant flux of $30 \text{ liter m}^{-2} \text{ hr}^{-1}$ (LMH), with an increase in pressure
 329 corresponding to membrane fouling. As can be seen, when no potential was applied, the pressure

required to maintain the constant flux increased from 1.5 to 3.1 psi over the course of 5 hours. In contrast, when the membrane was used as a cathode the pressure increased to 2.4 and 2.2 psi when the whole cell potential was 3 V and 5 V, respectively. The UF feed (reactor effluent) water quality in all UF experiments can be seen in Table 2. In these experiments, water quality properties were maintained constant by recycling the membrane permeate back to the feed. To ensure reproducibility, the membranes were cleaned between each run to ensure that the DI water permeability was similar to the initial conditions.

Figure 5. Impact of applied electrical potential on the required pressure to maintain a steady flux with (a) constant feed concentrations, and (b) system operated at 90% recovery. Experimental conditions were: aSBR effluent as feed, cross flow velocity of 20 cm/s, constant flux of 30 LMH (a) and 40 LMH (b). Electrical potentials in the Figure represent the whole cell potential (potential difference between membrane (used as cathode) and counter electrode (anode)). In (a), blue (triangle) and red (cycle) lines represent the case where the membrane was used as a cathode with 5 V and 3 V applied to the membrane and counter electrode, respectively; the black (square) line corresponds to the control (0 V). In (b), the red (cycle) line corresponds to the case where the membrane was used as a cathode (5 V) and the black (square) line represents the

control (0 V). All experiments were done in triplicate, with error bars representing 95% confidence intervals.

Table 2. Water quality parameter

Parameter	Reactor Effluent	UF Permeate	NF Permeate
Total Organic Carbon (ppm)	26.5±4	22.5±5	4.8±0.4
Chemical Oxygen Demand (ppm)	96.5±12	60±10	3±3
Turbidity (NTU)	16±2	0.9±0.5	< 0.1
Conductivity (µS/cm)	1260±461	1111±314	129±31
Volatile Suspended Solid (VSS) (ppm)	13.7±1.8	ND*	ND*
Total Suspended Solid (TSS) (ppm)	16.2±2.4	4±4	ND*
VSS/TSS (%)	86 ± 4	ND*	ND*

*ND means the parameter is not detectable

In an attempt to simulate real-world conditions, a second set of experiments were performed where the membrane permeate was not recirculated, which resulted in the increased concentration of the feed solution over time. Here, the membrane was operated at a constant flux of 40 LMH, and the pressure was monitored over time when the membrane was used as a cathode (5 V cell potential) or under no potential conditions (0 V) (Figure 5b). The system was operated at 90% recovery, i.e. until the feed volume reached 10% of its initial value. As can be seen, the application of 5 V to the system (membrane as cathode) resulted in significantly better performance. When no potential was applied, the system reached a final pressure of 17 psi in order to maintain a constant flux of 40 LMH. In contrast, when an electrical potential was applied, the system only required 7 psi to maintain that flux.

3.4 Treating aSBR Effluent with Electrically Charged UF Membranes

Based on the results seen in Figure 5, it was decided that to effectively treat the aSBR effluent with the UF membrane while maintaining minimal fouling, the membrane would operate in a decreasing flux mode. In this mode, the system was run at 90% recovery, where membrane permeate was collected and not returned to the feed. Additionally, the flux was adjusted to the feed concentration, such that the initial flux (30 LMH) was reduced by 2 LMH for every 20% recovery. Thus, the final flux (when the system is approaching 90% recovery) would be 22 LMH (Figure 6a). In addition, the membrane was backwashed with UF permeate for one minute every half hour; no further cleaning of the membrane was performed. In this series of experiments, three decanted volumes from the aSBR were treated consecutively under each set of experimental conditions. The application of 5 V to the membrane and counter electrode (membrane as a cathode) had a significant impact on membrane fouling, with the pressure increasing from 1.5 psi to 2.2 psi over the course 65 hours, which was the length of time needed to treat three decanted volumes with 90% recovery (Figure 6b). In contrast, when no potential was applied, the final pressure was nearly 7 psi, which is over three times higher than the case where the membrane was used as a cathode (Figure 6b). Interestingly, when the membrane was used as a cathode (5 V), but switched to an anode (1.5 V) during backflushing events, the membrane experienced very rapid fouling (Figure 6b). In fact, the fouling was so rapid (and irreversible) that the experiment was aborted at the end of the second round of aSBR effluent treatment. This result confirmed that the majority of foulants in the aSBR decanted effluent were negatively charged since they rapidly and irreversibly attached to the membrane surface when it was positively charged; it is possible that in addition to electrostatic adsorption, oxidizing

conditions generated by the membrane anode could lead to electropolymerization of the organic molecules on the membrane surface, which could lead to irreversible membrane fouling.

Figure 6. Treating aSBR effluent with electrically conducting UF membranes. (a) Flux as a function of feed concentration (up to 90% recovery). (b) Pressure required to maintain a given flux under different electrical conditions when system was operated at 90% recovery. Experimental conditions were: aSBR effluent as feed, cross flow velocity of 20 cm/s, membrane was backwashed with permeate every 30 minutes for 1 minute. Red (cycle) line represents conditions when membrane was used as cathode with 5 V applied to the membrane/counter electrode; blue (triangle) line represents conditions when the membrane was used as a cathode (5 V) and as an anode (1.5 V) during backwashing events; black (square) line represents the control (0 V).

UF permeate water quality parameters are summarized in Table 2. Not surprisingly, the UF membrane treatment had a modest impact on TOC levels, which decreased from 26.5 ± 4 to 22.5 ± 5 ppm. Based on previous literature and our HPLC analysis, it is expected that the majority of the organic compounds in the aSBR effluent are small organic molecules, which would pass through a UF membrane [6]. However, the UF membrane treatment did have a dramatic impact on TSS and turbidity levels, reducing them from 16.2 ± 2.4 ppm to 4 ± 4 ppm, and from 16 ± 2

NTUs to 0.9 ± 0.5 NTUs, respectively (Table 2). COD levels in the UF permeate were 37% lower than in the feed. No statistical significance was found in COD levels between the UF permeate or retentate generated from the charged and uncharged membranes (Figure 7). Thus, this water is suitable as NF feed due to its low TSS and turbidity levels.

Figure 7. COD concentrations measured in the different UF streams. Measurements were triplicated, with error bars representing 95% confidence intervals.

3.5 NF Membrane Performance – NF Fouling

UF permeate was used as feed water for the NF membranes. In these experiments, the system was operating in concentration mode, where membrane permeate was not returned to the feed, and the feed was allowed to concentrate over time (90% recovery). NF membranes were operated at a constant pressure (180 psi), with flux decline indicating membrane fouling. Interestingly, fouling in the NF system was not sensitive to the application of an electrical potential to the membrane surface, with nearly identical fouling rates observed when the membrane was charged with 5 V (as cathode), 0 V, or 1.5 V (as anode) (Figure 8). NF permeate had excellent water quality, with non-detectable TSS and turbidity levels, and near zero TOC and

COD values (4.8 ± 0.4 and 3 ± 3 ppm, respectively) (Table 2). We speculate that the negligible impact of the electrical potential on membrane fouling is caused by the nature of the foulants that pass through the UF membrane. Since the majority of organic molecules found in the aSBR effluent (which is used as UF feed) are negatively charged, they are repelled by the negatively charged UF membranes. Thus, molecules that do pass through the UF membrane are likely to be neutral or positively charged, which would make them immune to the enhanced electrostatic forces generated during the application of an electrical charge on the NF surface [24].

Figure 8. Fouling of electrically conducting NF membranes under different applied potentials. Experimental conditions: feed water was UF permeate, cross flow velocity was 20 cm/s, pressure was 180 psi. The red (cycle) line corresponds to conditions when the membrane was used as an anode (1.5 V); the blue (triangle) line represents conditions when the membrane was used as a cathode (5 V); the black (square) line represents the control (0 V).

3.6 NF Recovery

After the fouling experiments, an attempt was made to recover membrane performance by flowing DIW across the fouled membrane surface at a cross-flow velocity of 20 cm/s; the DIW

was continuously recycled. Interestingly, when the membrane was used as an anode during cleaning (1.5 V), the cleaning process was not successful in restoring membrane flux to its original value, with the flux recovering to only 16 LMH, only 57% of its initial value (28 LMH) (Figure 9). In contrast, when the membrane was used as a cathode (5 V), or when no potential was applied, nearly full flux recovery was observed, with the flux returning to its original value. It is possible that under anodic conditions some of the deposited organic matter underwent polymerization, which led to irreversible membrane fouling [28, 38].

Figure 9. NF membrane recovery. Recovery was performed by flowing DIW over the membrane at 20 cm/s at a pressure of 180 psi while measuring flux. Red (circle) line represents conditions when membrane was used as anode (1.5 V); blue (triangle) line represents conditions when membrane was used as cathode (5 V); black (square) line represents the control (0 V). Experiments were duplicated with error bars representing 95% confidence intervals.

3.7 Economic Analysis

Energy consumption associated with the application of 5 V to the UF membrane system was determined to be 0.01 kWh/m². This was calculated by measuring the current density on the

membrane (0.2 mA/cm^2) and multiplying this value by the potential (5 V) to get the power density (10 W/m^2). During the UF treatment, the average flux of the system was 26 LMH. Based on this value, it was calculated that the energy consumption per cubic meter of UF permeate was 0.4 kWh/m^3 . Assuming average commercial energy costs in CA (averaged over winter and summer - $\$0.2/\text{kWh}$), the additional cost associated with the application of the electrical potential is $\$0.076/\text{m}^3$ of treated water.

4. Conclusions

In this paper we demonstrate the use of an aSBR coupled to a UF and NF membrane system for the purpose of treating high-strength industrial wastewater with intermittent flow containing benzyl alcohol – a commonly used paint stripper. The aSBR is demonstrated to be able to effectively degrade the organic contaminant (80-90%) over a 24 hour period, producing effluent that is relatively low in COD. Furthermore, we demonstrate the advantages associated with the use of electrically charged membranes for the treatment of anaerobic reactor effluent. When the UF membrane is used as a cathode (5 V), long-term experiments show that the membrane experiences very little fouling while continuously producing high quality effluent. In contrast, if the UF membrane is uncharged, significant fouling occurs and system performance is compromised, which could lead to an increase in chemical cleaning events. In contrast to the UF membranes, NF membrane fouling was not impacted by the application of an electrical potential. However, when attempting to recover the lost flux on the NF membranes, positively charged NF membranes were not completely recovered, which is likely due to polymerization of fouling molecules on the NF surface. The negatively charged and uncharged NF membrane's flux was recoverable after a simple rinse with DIW. The water treatment system described here yielded treated water with an excellent quality that can be readily discharged or reused. Importantly, the

enhanced anti-fouling capabilities of the electrically charged UF membranes will significantly reduce the need for chemical cleaning, as well as the cost of the overall process.

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Reference

- [1] Y.J. Chan, M.F. Chong, C.L. Law, D. Hassell, A review on anaerobic–aerobic treatment of industrial and municipal wastewater, *Chemical Engineering Journal*, 155 (2009) 1-18.
- [2] R.E. Speece, Anaerobic biotechnology for industrial wastewater treatment, *Environmental science & technology*, 17 (1983) 416A-427A.
- [3] L.T. Angenent, K. Karim, M.H. Al-Dahhan, B.A. Wrenn, R. Domíquez-Espinosa, Production of bioenergy and biochemicals from industrial and agricultural wastewater, *TRENDS in Biotechnology*, 22 (2004) 477-485.
- [4] F. Cakir, M. Stenstrom, Greenhouse gas production: a comparison between aerobic and anaerobic wastewater treatment technology, *Water Research*, 39 (2005) 4197-4203.
- [5] J. Heider, G. Fuchs, Anaerobic metabolism of aromatic compounds, *European Journal of Biochemistry*, 243 (1997) 577-596.
- [6] O. Todini, L.H. Pol, Anaerobic degradation of benzaldehyde in methanogenic granular sludge: the influence of additional substrates, *Applied microbiology and biotechnology*, 38 (1992) 417-420.
- [7] G. Tchobanoglous, J. Darby, K. Bourgeois, J. McArdle, P. Genest, M. Tylla, Ultrafiltration as an advanced tertiary treatment process for municipal wastewater, *Desalination*, 119 (1998) 315-321.
- [8] M. Gómez, A. De la Rua, G. Garralón, F. Plaza, E. Hontoria, M. Gómez, Urban wastewater disinfection by filtration technologies, *Desalination*, 190 (2006) 16-28.
- [9] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, *Desalination*, 216 (2007) 1-76.

499 [10] T. Wintgens, M. Gallenkemper, T. Melin, Endocrine disrupter removal from wastewater using membrane
500 bioreactor and nanofiltration technology, *Desalination*, 146 (2002) 387-391.

501 [11] J.-H. Choi, S. Dockko, K. Fukushi, K. Yamamoto, A novel application of a submerged nanofiltration
502 membrane bioreactor (NF MBR) for wastewater treatment, *Desalination*, 146 (2002) 413-420.

503 [12] S. Ognier, C. Wisniewski, A. Grasmick, Membrane bioreactor fouling in sub-critical filtration conditions: a
504 local critical flux concept, *Journal of Membrane Science*, 229 (2004) 171-177.

505 [13] K.-H. Choo, C.-H. Lee, Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor, *Water*
506 *Research*, 30 (1996) 1771-1780.

507 [14] I.-S. Chang, P. Le Clech, B. Jefferson, S. Judd, Membrane fouling in membrane bioreactors for wastewater
508 treatment, *Journal of environmental engineering*, 128 (2002) 1018-1029.

509 [15] W. Guo, H.-H. Ngo, J. Li, A mini-review on membrane fouling, *Bioresource technology*, 122 (2012) 27-34.

510 [16] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of
511 nanofiltration membranes, *Journal of membrane science*, 132 (1997) 159-181.

512 [17] S. Hong, T. Bae, T. Tak, S. Hong, A. Randall, Fouling control in activated sludge submerged hollow fiber
513 membrane bioreactors, *Desalination*, 143 (2002) 219-228.

514 [18] A. Sofia, W. Ng, S. Ong, Engineering design approaches for minimum fouling in submerged MBR,
515 *Desalination*, 160 (2004) 67-74.

516 [19] Z. Huang, S.L. Ong, H.Y. Ng, Submerged anaerobic membrane bioreactor for low-strength wastewater
517 treatment: effect of HRT and SRT on treatment performance and membrane fouling, *Water research*, 45 (2011) 705-
518 713.

519 [20] B. Cho, A. Fane, Fouling transients in nominally sub-critical flux operation of a membrane bioreactor, *Journal*
520 *of membrane science*, 209 (2002) 391-403.

521 [21] L. Liu, J. Liu, B. Gao, F. Yang, Minute electric field reduced membrane fouling and improved performance of
522 membrane bioreactor, *Separation and Purification Technology*, 86 (2012) 106-112.

523 [22] L. Liu, J. Liu, B. Gao, F. Yang, S. Chellam, Fouling reductions in a membrane bioreactor using an intermittent
524 electric field and cathodic membrane modified by vapor phase polymerized pyrrole, *Journal of Membrane Science*,
525 394 (2012) 202-208.

- [23] C.-F. de Lannoy, D. Jassby, K. Gloe, A.D. Gordon, M.R. Wiesner, Aquatic biofouling prevention by electrically charged nanocomposite polymer thin film membranes, *Environmental science & technology*, 47 (2013) 2760-2768.
- [24] A.V. Dudchenko, J. Rolf, K. Russell, W. Duan, D. Jassby, Organic fouling inhibition on electrically conducting carbon nanotube–polyvinyl alcohol composite ultrafiltration membranes, *Journal of Membrane Science*, 468 (2014) 1-10.
- [25] A. Ronen, W. Duan, I. Wheeldon, S.L. Walker, D. Jassby, Microbial attachment inhibition through low voltage electrochemical reactions on electrically conducting membranes, *Environmental Science & Technology*, (2015).
- [26] W. Duan, A. Dudchenko, E. Mende, C. Flyer, X. Zhu, D. Jassby, Electrochemical mineral scale prevention and removal on electrically conducting carbon nanotube–polyamide reverse osmosis membranes, *Environmental Science: Processes & Impacts*, 16 (2014) 1300-1308.
- [27] G. Gao, C.D. Vecitis, Electrocatalysis aqueous phenol with carbon nanotubes networks as anodes: Electrodes passivation and regeneration and prevention, *Electrochimica Acta*, 98 (2013) 131-138.
- [28] A.M. Zaky, B.P. Chaplin, Porous substoichiometric TiO₂ anodes as reactive electrochemical membranes for water treatment, *Environmental science & technology*, 47 (2013) 6554-6563.
- [29] W.E. Federation, A.P.H. Association, Standard methods for the examination of water and wastewater, American Public Health Association (APHA): Washington, DC, USA, (2005).
- [30] C.-F. de Lannoy, D. Jassby, D. Davis, M. Wiesner, A highly electrically conductive polymer–multiwalled carbon nanotube nanocomposite membrane, *Journal of Membrane Science*, 415 (2012) 718-724.
- [31] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *Journal of membrane science*, 188 (2001) 115-128.
- [32] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: II. Membrane physiochemical properties and their dependence on polyamide and coating layers, *Desalination*, 242 (2009) 168-182.
- [33] M. Jahanshahi, A. Rahimpour, M. Peyravi, Developing thin film composite poly (piperazine-amide) and poly (vinyl-alcohol) nanofiltration membranes, *Desalination*, 257 (2010) 129-136.
- [34] Metcalf, Eddy, *Wastewater Engineering: Treatment and Resource Recovery*, McGraw-Hill international ed., 2014.

- 554 [35] A. Ramesh, D.-J. Lee, S. Hong, Soluble microbial products (SMP) and soluble extracellular polymeric
555 substances (EPS) from wastewater sludge, *Applied microbiology and biotechnology*, 73 (2006) 219-225.
- 556 [36] Y. He, P. Xu, C. Li, B. Zhang, High-concentration food wastewater treatment by an anaerobic membrane
557 bioreactor, *Water research*, 39 (2005) 4110-4118.
- 558 [37] J.-H. Shin, S.-M. Lee, J.-Y. Jung, Y.-C. Chung, S.-H. Noh, Enhanced COD and nitrogen removals for the
559 treatment of swine wastewater by combining submerged membrane bioreactor (MBR) and anaerobic upflow bed
560 filter (AUBF) reactor, *Process biochemistry*, 40 (2005) 3769-3776.
- 561 [38] A.M. Zaky, B.P. Chaplin, Mechanism of p-Substituted Phenol Oxidation at a Ti4O7 Reactive Electrochemical
562 Membrane, *Environmental science & technology*, 48 (2014) 5857-5867.

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