Environmental Science
Water Research & Technology

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Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-06-2020-000608.R1
Article Type:	Paper

Water Impact Statement

Anaerobic membrane bioreactors (AnMBRs) have the potential to be a sustainable wastewater treatment platform by enabling water reuse, nutrient recovery, and energy generation, but is still mired by problems of membrane fouling. This study provides much needed pilot-scale demonstration of fouling management strategies and develops proactive field-deployable methods for fouling control.

Dynamic monitoring and proactive fouling management in a pilot scale gas-sparged anaerobic membrane bioreactor

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Abstract

This study examines membrane performance data of a pilot-scale gas-sparged Anaerobic Membrane Bioreactor (AnMBR) over its 472-day operational period and characterizes the foulant cake constituents through a membrane autopsy. The average permeability of 336±81 LMH/bar during the first 40 days of operation decreased by 92% by the study's conclusion. While maintenance cleaning was effective initially, its ability to restore permeability decreased with time. Wasting bioreactor solids appeared to be effective in restoring permeability where chemical cleans were unable to. The restoration mechanism appears to be a decrease in colloidal material, measured by semi-soluble chemical oxygen demand (ssCOD), rather than bioreactor total solids concentration. This is further supported through the use of fluorometry during AnMBR operation, which showed an increase in tyrosine-like compounds during heavy fouling conditions, suggesting that proteinaceous materials have a large influence on fouling. This was corroborated during membrane autopsy using Fourier Transform Infrared Spectroscopy (FTIR). FTIR, scanning electron microscopy with energy dispersive x-ray spectroscopy, and transmission electron microscopy were used to characterize inorganic scalants and predominantly found phosphate salts and calcium sulfate. Fundamentally characterizing foulants and introducing novel and dynamic monitoring parameters during AnMBR operation such as ssCOD and fluorometry can enable more targeted fouling control.

Keywords
Anaerobic membrane bioreactor
Membrane fouling
Biofouling
Inorganic scaling

1. Introduction

Anaerobic membrane bioreactors (AnMBRs) have become an increasingly appealing wastewater treatment technology that combine anaerobic treatment and membrane filtration. This pairing confers many advantages towards treatment effectiveness, allowing the system to operate at high solids retention times (SRT) to help achieve high rates of chemical oxygen demand (COD) removal, and ultimately producing a reuse-quality effluent along with low biosolids concentrations.[1,2] These characteristics have led to its application in industrial settings, such as breweries, and has generated significant research interest for use in domestic wastewater treatment.[3–5] Despite the huge potential, the widespread adoption of AnMBR technology has been limited, largely due to concerns of membrane fouling.[1,6] Membrane fouling involves physicochemical interactions between the biological sludge, wastewater matrix, and membrane material that results in a reduction of permeate flux at constant transmembrane pressures (TMP) or an increase in TMP at constant flux.[7,8] While membrane fouling has been a key challenge for membrane bioreactors overall, the issue is especially pronounced in AnMBRs, which has lower sludge filterability than in aerobic systems.[6,9] Due to the severity of fouling issues, membrane maintenance in AnMBRs can account for over 50% of the energy demand of AnMBR operation, indicating a need for optimization.[4]

The foulants can be divided into biotic and organic agents, often considered the primary cause of fouling, and inorganic foulants such as metal ions, also referred to as scalants.[7] The major biotic components include microorganisms larger than 0.1 μm that are retained by both microfiltration (MF) or ultrafiltration (UF) membranes, as well as their associated extracellular polymeric substances (EPS) and soluble microbial products (SMP), which can form biofilms and negatively impact membrane performance and make maintenance more difficult.[7,9] Scaling,

while drawing less research attention than biotic factors, has been observed in AnMBRs, such as struvite ($MgNH_4PO_4 \cdot 6H_2O$) and $CaCO_3$ precipitating on membrane surfaces in previous studies.[10,11] While often separated into distinct categories, organic and inorganic fouling occur simultaneously; biopolymers can complex with metal ions and exacerbate the severity of fouling until it is irreversible.[12,13]

The mechanisms of fouling development can have a large impact on effectiveness of different methods for fouling management.[14] Cake layer formation describes the accumulation of solids at the membrane surface to the point where it blocks pores, and has been hypothesized as the predominant fouling mechanism, particularly during operation at higher fluxes.[15–17] Pore constriction is believed to occur due primarily to the adsorption of colloidal or soluble biopolymers and precipitation of inorganics within the pores of the membrane.[9,18,19] While the foulant cake layer tends to develop quickly, it is believed that pore clogging is primarily responsible for the long term, irreversible fouling experienced by membranes, particularly for UF membranes, and will occur inevitably, even during low flux operation.[16,19]

Effective membrane maintenance requires a combination of physical and chemical cleaning strategies to reverse the effects of fouling. The general objective of physical methods is to remove the sludge cake and potential biofilm deposits from the membrane surface, which would address cake layer formation. This is often the aim of water backflushing and membrane relaxation, both ubiquitous techniques for membrane maintenance.[7,20] In addition, configuration specific methods for imparting shear at the membrane surface, such as granular activated carbon fluidization and gas sparging, are often employed.[14,15] Gas sparging, which involves bubbling biogas through the bottom of the membrane tank to scour the sludge from the membrane surface has been the most common method for side-stream AnMBR configurations.[1,21]

Most physical cleaning methods are difficult to employ within the pores, necessitating the use of chemical backwashing to address pore clogging.[22] There are many different organic and inorganic species that can be adsorbed in the pores, often necessitating the use of a combination of various cleaning agents in tandem: commonly, HCl, H_2SO_4, and citric acid have been widely used to treat inorganics, NaOH and NaOCl have been used to treat organics and biofoulants, and various additives such as ethylenediamine tetraaceticacid (EDTA) and ammonium bifluoride have been added for the removal of metals through chelation.[23,24] Because the chemicals are foulant specific, it is critical to identify the mechanism of fouling and whether the foulant is organic or inorganic.[1,16] Furthermore the use of chemical cleaning agents is known to shorten the operational life of membranes, making it more critical for the appropriate cleaning agent to be used for a specific event.[7,22,25] Often times, the selection of cleaning chemicals for membrane bioreactors is empirically determined based on prior experiments, which demonstrates a need to characterize the foulants encountered during AnMBR operation in order to optimize chemical use, which would save on chemical costs and extend the membrane's life.[22,26] Characterization of the foulants is usually performed in end-of-life membrane autopsies and typically involve a combination of analytical techniques such as microscopy and spectroscopic techniques to determine the nature and composition of foulants.[27,28] Because these techniques require the opening up the membrane tank to sample membrane fibers, they are rather impractical to perform during regular operation, as sampling would likely expose the system to oxygen.

Because foulant characterization during operation is difficult, determining when and to what degree to deploy the fouling management techniques typically relies on operational parameters such as flux and TMP. The concept of flux as a key parameter in the mechanistic understanding of fouling has been largely influential since Field et al. (1995) proposed that in

clean water operation there theoretically exists a "critical flux," below which fouling does not occur; this is known as the "strong form" of the critical flux hypothesis.[29] Because real feedwater has solutes that can irreversibly adsorb onto the pores, however, a "practical form" of the critical flux hypothesis was developed, positing that a critical flux exists that allows for the operation without the need for membrane cleaning for extended periods of time (> 3 weeks).[14,30] From this hypothesis, it can be surmised that if an MBR were to be operated under subcritical flux conditions, pore constriction would be negligible in the short term, and solids deposition onto the membrane surface is the main mechanism that needs to be managed. While critical flux is the most discussed, there may be many "critical" parameters associated with membrane maintenance that have a threshold beyond which fouling occurs, such as a critical gas-sparging rate, which can serve as a guideline for a system's physical fouling control requirements.[7,21]

While responding to abrupt changes in the TMP and flux profiles during regular operation can help restore membrane performance, typically the reason for the changes is because fouling has already occurred. This highlights the need for proactive monitoring strategies that track indicators that suggest fouling events are likely to occur. As previous AnMBR studies have suggested that biosolids and their associated polysaccharides and proteins are the primary membrane foulants, dynamic monitoring methods that can measure these parameters, such as semi-soluble Chemical Oxygen Demand (ssCOD), a COD measurement performed on sample that has been filtered through a 1.2 μm filter paper, and fluorometric analyses during the system's normal operation can enable more proactive management strategies before severe fouling events are triggered.[13,31,32] This study examines the membrane performance, the impact of fouling, and the effectiveness of various physical and chemical control strategies in a pilot-scale AnMBR treating domestic wastewater located in Ft. Riley,

Kansas. In addition to managing fouling using flux and TMP and performing a traditional membrane autopsy for foulant characterization, the use of fluorometry and ssCOD are proposed as potential monitoring tools that can enable proactive fouling control during normal AnMBR operation. Synthesizing the findings from this diverse suite of analyses performed at the pilot scale can help refine maintenance strategies to more effectively target key foulants, improving overall system performance and its useful life expectancy.

2. Materials and Methods

The AnMBR was operated continuously for 472 days, treating domestic wastewater from Ft. Riley, Kansas, as has been described in previous publications.[33,34] A schematic of the pilot-scale AnMBR and its fouling control appurtenances is shown in Figure 1. Municipal wastewater from Ft. Riley was passed through a 1.7 mm screen (Eaton model DCF400, Dublin, Ireland) prior to being fed to the AnMBR, which operated at an average HRT of 11±3 hours and an average optimized SRT of 60±27 days. Sludge was recirculated between the bioreactor and the membrane tank using two progressive cavity pumps (Moyno model 33304, OH, USA) in order to promote mixing, with one of the pumps also being used to waste the sludge from the bioreactor. The membranes used in this study were Suez 500d UF polyvinylidene difluoride (PVDF) membranes with a pore size of 0.04 μm.

2.1 Fouling control

The fouling control strategy used in this study were primarily physical. Sparging was accomplished using a double-diaphragm gas blower (KNF model N0150.1.2, NJ, USA) to pump the biogas from the headspace of the bioreactor. The net sparge flow rate, measured in standard liters per minute (SLPM), was varied over the course of pilot operation through a series of experiments. Other physical control strategies included backpulsing and extended membrane

relaxation, during which permeate production, sludge recirculation, and gas-sparging were stopped.

Discrete chemical cleaning events were initiated either manually or on a user-defined automated schedule during high TMP events or in response to TMP instability. The chemical backpulse solutions used were 500 mg/L sodium hypochlorite (NaOCl) or 2000 mg/L citric acid, which could be employed either alone, or back-to-back. Maintenance cleans were initiated on a more regular basis, usually in response to high TMP events, and could involve using the chemicals either alone or back-to-back. The more intense recovery cleaning procedure was only used once throughout the operational period and involved extended chemical soaking periods using each chemical. Representative cleaning procedures for maintenance cleans and the recovery clean are shown in Table S.1 and Table S.2, respectively, and were based on manufacturer recommendations.

2.2 Fouling parameter analyses

TMP was measured as the difference in the pressure readings (in psig) between a pair of pressure transmitters (Endress and Hauser Cerabar PMC51, Reinach, Switzerland) located in the membrane tank's bulk sludge and from the permeate line. Flux was a derived parameter calculated from the permeate flow rate, taken using an electromagnetic flow meter (Endress and Hauser 5P1B15, Reinach, Switzerland), and dividing it by the total membrane surface area (12.9 m^2). Permeability is calculated as the ratio of flux to TMP and is presented in units of LMH/bar.[14,35] A baseline permeability was established by averaging the permeability during the period of virgin membrane operation (~ first 40 days of AnMBR operation), under stable conditions without the use of chemical cleaning. The percentage of baseline permeability data

was then calculated by dividing the permeability at any time point by the established baseline permeability.

Membrane permeate samples were collected for semi-soluble chemical oxygen demand (ssCOD) and fluorometry measurements. 500 mL of permeate was collected for each test in polypropylene bottles, and samples for ssCOD analyses alone were immediately acidified to a pH of below 2 with sulfuric acid on site. Samples were sparged with air for 10 minutes to eliminate the contribution of hydrogen sulfide and dissolved methane on the COD measurement and filtered through 1.2 μm filter paper, to exclude the effects of larger insoluble particles (Whatman 1822-047, Maidstone, United Kingdom). COD measurements were performed on these samples using Hach method 8000 and a Hach spectrophotometer (Hach DR3900, CO, USA). The samples were aliquoted in quartz cuvettes (Starna 3-Q-10, Ilford, UK) and analyzed using a Horiba Aqualog fluorometer (Horiba, Kyoto, Japan) to generate excitation-emission matrices (EEMs).

Membrane fibers were collected at the end of operation for autopsy analyses. American Water Chemicals, Inc (AWC, FL, USA) performed a membrane autopsy, which included Loss on Ignition (LOI) testing to determine the organic content of the foulants, scanning electron microscopy (SEM) (Hitachi SU5000 Tokyo, Japan) with energy dispersive x-ray spectroscopy (EDX) (Bruker XFlash 6 | 60, MA, USA) to determine the elemental composition of the foulants, and Fourier Transform Infrared Spectroscopy (FTIR) (PerkinElmer Spectrum 100, MA, USA) to analyze functional groups. Foulant samples for SEM were each scraped from various locations along the length of the membrane fiber, mounted onto carbon tape, and then imaged. Areas of interest identified from the micrograph were then analyzed using EDX. FTIR sample preparation required collecting multiple fibers from different areas of the module in order to obtain a

representative bulk sample. Foulant cake from the individual fibers were all scraped into a single container with a plastic spatula to collect the bulk foulant, then residual foulant was rinsed off of the fibers with deionized water into the bulk. The foulant was then mixed and then dehydrated at 105^0C for 8 hours. A portion of this dehydrated foulant was used for FTIR analysis, while the remaining was fired at 450^0C for 8 hours to combust any organics present in the sample. This combusted sample was used for the LOI test as well as for another FTIR analysis that focuses on the inorganic components of the foulant cake.

In addition to the analyses done by AWC, transmission electron microscopy (TEM) and Selected Area Electron Diffraction (SAED) analyses were performed at Kansas State University's Microscopy Facility (FEI/Philips CM 100, OR, USA) using a tungsten filament.

3. Results and discussion

3.1 Membrane Performance

Over the 472-day operation period, the AnMBR operated at an overall average net flux of 7.6±1.6 L m^{-2} h^{-1} (LMH) and an average TMP of 13±9 kPa (Figure S1). The first 40 days of operation were used to establish a baseline for the system's membrane performance without the use of chemical cleaning; the average permeability during this period was 336±81 LMH/bar, with an average flux of 10.1±2.2 LMH, net biogas sparge flowrate of 75 SLPM, and average TMP of 2.7±1.0 kPA (Figure 2A). The ability to operate for long periods, previously defined as over three weeks, without any maintenance cleaning is consistent with the practical definition of subcritical flux operation, during which solids deposition is minimal.[30] The maintenance clean executed on day 42 was able to recover 80% of the baseline permeability, suggesting that no appreciable irreversible fouling had occurred, and that the system was being operated under subcritical conditions.

The permeability decreased by 92% from the start of operation to an average permeability to 28±6 LMH/bar in the last 40 days of operation (Figure 2B). The first irreversible reduction in permeability coincided with a user-controlled net biogas sparge flowrate reduction to 37 SLPM, initiated on day 56, while maintaining a flux setpoint of 10 LMH (Figure 2A). Subsequent attempts to recover the baseline permeability by increasing biogas sparge flowrate were not able to be sustained, suggesting that physically irremovable fouling had occurred, and that the system was operating below the critical sparging rate, and that solids deposition had occurred due to the reduced sparging rate. The presence of irremovable fouling has been hypothesized to increase the propensity for local fouling and consequently lower the critical flux of the overall system, which lowers the overall membrane permeability.[21,30] Lowering the flux setpoint from 10 LMH to 6.8 LMH on day 74, while still operating at the reduced sparging rate of 37 SLPM, was able to restore stable membrane performance without chemical cleaning or any other parameter adjustments, further supporting the critical sparging rate hypothesis. Thus, managing the initial deposition of foulants appears to be critical for maintaining membrane performance.

3.1.1 Chemical Cleaning The first major reduction in permeability occurred between days 40 to 42, and prompted a maintenance clean that was able to recover nearly all of the lost permeability (Figure 2A). Although the cleaning procedure occurs within 40 minutes from initiation to resuming normal operation, the maximum recovery of permeability appears to be slightly delayed, occurring 7 days following the cleaning event (Figure 2A). This delayed recovery was observed following each chemical cleaning event that was initiated after an extended period (more than 3 weeks for subcritical conditions) without any maintenance cleans (days 42, 84, and 114, as shown in Figure 2B), with the maximum recovered permeabilities being observed 6±2

days after the respective clean initiation time, on average.[30] This effect is less pronounced during periods of regular maintenance cleaning. One possibility is that the final water backpulsing during each clean may not have been sufficient for removing the partially dissolved foulants from the pores or the membrane surface, and that the physical mechanism of biogas sparging likely gradually completes this process in the days after the cleaning. Regular maintenance cleans may interrupt the solids deposition onto the cake layer to the point where the physical removal mechanisms do not have as large of an impact on recovering permeability.

The effectiveness of the maintenance cleans also decreased progressively with time; cleaning events recovered 80%, 34%, 7%, and 2% of the baseline permeability on days 42, 84, 114, and the final clean on day 461, respectively, indicating that the foulant becomes less susceptible to chemical cleans as AnMBR operation continues (Figure 2B). The reasons for this progression of irreversible fouling require further investigation and may have implications on fouling control strategies. One possible reason is that the foulants that the chemical cleaning agents used in this study were ineffective against were not able to be removed, leading to their gradual accumulation over the system's operation. Elucidating the main foulants at each stage of the membrane's operational life may lead to more targeted control strategies aimed at specific fouling agents.

3.1.2 Bioreactor Solids and Semi-Soluble COD Chemical cleaning, even when used regularly, was not always able to considerably recover permeability, as observed from days 210 to 270, where permeability was unstable and relatively low despite regular maintenance cleaning (Figure 3A). Some fouling events appear to be correlated with bioreactor solids concentration or ssCOD. The largest recovery of permeability occurred from days 299 to 316, where the solids wasting caused a 64% decrease in bioreactor TS and an 80% decrease in ssCOD concentrations,

recovering 34% of the baseline permeability, significantly more effective than chemical cleaning during this period of operation. The system was operated from day 323 to day 411 with solids wasting at a rate of 2% of the bioreactor volume per day as the only control strategy actively being employed, without any maintenance cleans. TMP stability seemed to be improved at lower ssCOD concentrations as well, indicating more consistent membrane performance.

The large wasting event did lead to a temporary period of decreased treatment performance for 55 days following the loss of biomass; it is likely that this performance loss could have been avoided had the sludge wasting been conducted periodically, rather than all at once.[33] Nonetheless, treatment performance was able to be recovered without any additional action aside from regular operation.

The role of solids in MBR fouling has been controversial; while many studies have shown that increasing solids concentrations has a negative impact on membrane performance, several others have shown that the effect is negligible or even positive.[20,36] In a previous AnMBR study, Dagnew et al. (2012) found the impact of solids concentrations less than 20 g/L were due mostly to colloids and the solids, as a whole, would have negligible impact when operating at subcritical fluxes.[37] The average bioreactor TS during the system's operation was 9200±6000 mg/L, well below 20 g/L. Because of this, it is likely that the improved membrane performance was due to the reduction of ssCOD concentration rather than the TS concentration. Additionally, while ssCOD and TS concentrations typically mirror each other, this is not always the case as seen from day 321 to day 341 and day 458 to day 472 (Figure 3A). Furthermore, the permeability during those periods appear to recover when ssCOD decreased even as solids increased, suggesting that ssCOD may influence fouling behavior more than solids. The similar response in ssCOD and solids concentrations to wasting events may help to explain why

managing the solids has appeared to have mixed results in previous AnMBR studies, but with the majority of the studies not capturing the effects of colloids, further studies are required to confirm this.

A preliminary characterization of the colloidal fraction was conducted using a fluorometer to analyze the dissolved organic compounds in the permeate during days 452 and 472, which correspond to a period of decreased membrane performance and a period of stable membrane performance, respectively (Figures 3B and 3C). The fouling event occurring during day 452 appears to be caused by higher concentrations of proteinaceous materials, particularly tyrosine-like compounds, as indicated by the higher concentrations of the B2 fluorophore compared to what was observed on day 472.[38,39] Tryptophan-like and humic-like compounds, as indicated by fluorophores T1 and M, respectively, are present in both EEMS, but their impacts are relatively masked due the higher concentrations of tyrosine-like compounds.[38,39] Further research is required to confirm if colloidal proteinaceous materials have a disproportionate impact AnMBR fouling, and if they can be candidates for continuous monitoring in the membrane permeate. Another parameter that warrants future investigation is organic carbon measurements, which can be correlated with fluorometry results and has proven to be a powerful predictor for reverse osmosis biofouling.[40,41]

3.2 Foulant Characteristics and Composition

3.2.1 Organic Foulants The foulant layer contained black and brown clay and silt-sized particles, with an organic matter content of 59%, as determined by the LOI test. Organic filaments consistent with those of filamentous bacteria were observed only in samples taken from the bottom of the membrane module, indicating that the spatial distribution of foulants is non-uniform and may have implications for maintenance procedures. Annelids and algae were also

found throughout the cake layer, and although their impact on fouling is unknown, it indicates that the cake layer is a complex matrix governed by more than just biofilm properties.

FTIR analysis of the foulant cake (Figure 4A) confirmed that the fouling was largely organic. The strong peak at 1029.33 cm^{-1} has previously been suggested to be primarily polysaccharides in previous AnMBR studies, as polysaccharide and polysaccharide-like organic substances are found in the 900 cm^{-1} to 1200 cm^{-1} range.[42–45] However, a similar peak can be observed in the FTIR spectra from the ignition residue (Figure 4B), which suggests that the peak may be primarily inorganic in nature; the peak is consistent with spectra obtained from crystalline silica and the actual peak may be signatures of aluminosilicate materials, as well as phosphates and calcium sulfate.[46] The peaks at 1538.16 cm^{-1} and 1632.48 cm^{-1} are consistent with amide II and amide III groups, respectively, which have been noted for being unique to secondary protein structure and indicative of proteins in the foulant cake.[47,48] The peak at 3279.55 cm^{-1} is also associated with proteins, and suggests primary amine or amide.[49] The two peaks at 2920.27 cm^{-1} and 2851.21 cm^{-1} indicate the presence of saturated aliphatic compounds, which have also been observed to be present in urease protein samples [46,49]. Altogether, the FTIR analysis of the foulant cake corroborates the EEM analysis and suggests that proteins are the primary foulant on the AnMBR membrane fibers, which is consistent with previous AnMBR studies.[32,50]

3.2.2 Inorganic Foulants Inorganic scaling was observed using SEM-EDX and TEM. The main elements, excluding carbon, and oxygen, found were fluorine, which is associated with the membrane material (PVDF), silicon, calcium, iron, phosphorus, sulfur, sodium, aluminum, magnesium, titanium, potassium, whose average atomic percentages are listed in Figure 5A. The most commonly encountered precipitates were calcium sulfate, phosphate salts (primarily

calcium and iron phosphates), iron hydroxide, and titanium oxide. Notably, calcium carbonate formation was not observed using FTIR or microscopic methods, despite it being prevalent in previous AnMBR studies and MBRs in general.[51,52] The lack of calcium carbonate fouling in the system is further supported by an average Langelier Saturation Index (LSI) of -0.20±0.3 during the first 100 days of operation (Figure S3). However, because the LSI is specific to calcium carbonate, it does not preclude the possibility of scaling due to other calcium precipitates such as calcium sulfate and calcium phosphate.

Sulfur precipitation was observed primarily as calcium sulfate. Calcium sulfate's presence was readily found throughout the vertical profile of the membrane, and its presence was confirmed independently through SEM-EDX and TEM-SAED (Figures 5, Figure S3, and Figure S4). The only heavy metal-sulfur precipitate that was observed was one particle of zinc sulfide, which is in contrast with previous lab-scale studies which suggested that the increase in sulfur concentration in the foulant cake was due to heavy metal-sulfide precipitates, particularly FeS.[42,48]

While metal-sulfide precipitates were not found, phosphate minerals were found throughout the entire vertical profile of the membrane. Calcium phosphate was ubiquitous along the membrane module's entire profile, consistent with observations and modeling done on previous AnMBR studies that suggest phosphate was the strongest competitor for calcium ions and may be the dominant scalant in AnMBRs.[25,27] Aluminum phosphate was also observed, but only in samples from the top of the membrane module. The ubiquity of phosphate precipitates along with the lack of phosphorus accumulating organisms in the microbial community analysis shown in the final report on the system suggests that the observed phosphorus removal in the AnMBR is abiotic in nature.[33,46]

322 *3.3 Implications and Considerations for AnMBR Design and Operations*

323 The findings of this study suggest several possible improvements for optimizing
324 membrane fouling strategies in AnMBRs in future as a result of a more fundamental
325 characterization of the foulants. One of the main findings of this study was that the chemical
326 cleaning was not consistently effective, suggesting that the design and operation strategies could
327 be improved upon. In this study, the system tended to be operated at subcritical fluxes, which
328 implies that the gas sparging rates and fluid dynamics were not as favorable for solids deposition.
329 When the blower rate was decreased beyond the critical rate and the operating flux likely
330 exceeded the critical flux, neither chemical cleaning nor increasing the sparging rate were able to
331 restore the lost permeability. This indicates the need for proper, targeted remedial actions to the
332 different types of fouling events.

333 One of the design assumptions that was challenged was the composition of the foulants,
334 which dictated the choice of chemical cleaning agents. The 2000 mg/L citric acid was selected
335 for inorganic fouling control under the assumption that calcium carbonate would be the main
336 scalant, but both the LSI (Table S1) and the end-of-life membrane analyses suggested that
337 calcium carbonate was undersaturated and not precipitating on the membranes. Instead, as
338 verified by SEM-EDX and TEM, calcium sulfate and calcium phosphate were ubiquitous. While
339 citric acid is an effective antiscalant for calcium sulfate control when administered at
340 concentrations above 2500 mg/L, it has been observed to encourage calcium sulfate crystal
341 growth at concentrations below 2500 mg/L, suggesting that the 2000 mg/L citric acid chemical
342 cleans employed in this study may have actually had a negative impact on membrane
343 performance.[53,54] Citric acid has also been shown to have mixed results in removing calcium
344 phosphate scales as well, with several alternatives, such as mellitic acid or hydroxyethylene

diphosphoric acid, being far more effective.[55–57] It is possible that the chemically irreversible fouling in this study were due to cleaning agent selection, and that more targeted cleaning strategies may have been more suitable for recovering permeability, highlighting the importance of AnMBR foulant characterization.

The large improvements to membrane permeability as a response to solids wasting increases the priority of managing proteinaceous foulants. The presence of proteinaceous foulants in this system was independently corroborated through FTIR and fluorometry, and ssCOD may be a simple method for regularly monitoring their approximate concentration. Furthermore, it is hypothesized that ssCOD may explain the controversial findings of using solids as a predictor of membrane fouling. This could pave the way for a proactive fouling monitoring and management strategy which can have big impacts on long term AnMBR fouling management.

Previous studies have shown that the proteinaceous foulants were primarily from EPS [32]. Should this be the case, then the sludge wasting could improve membrane permeability through two mechanisms: the permeability could improve as a response either to the decrease in ssCOD or protein concentration, or the change in SRT can select for microbes that produce EPS with different properties and impacts to fouling.[58,59] The SRT response in this study can be found in the Supporting Information (Figure S2). Further studies are required to verify that the protein foulants are primarily associated with EPS, and what the primary mechanism is for improved membrane performance resulting from solids wasting.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

This work was supported by the Department of Defense Environmental Security Program [ESTCP Project number ER-201434]; and the U.S. Environmental Protection Agency under U.S. Army Corps of Engineers Humphreys Engineering Service Center [Contract W912HQ-15-C-0001]. Graduate student research was also supported by the National Science Foundation CBET Environmental Engineering (Program # 1440) award # 1805631 and the NSF National Research Traineeship (NRT) award # 1828571. The authors would also like to acknowledge Dr. Daniel Boyle for providing his expertise on transmission electron microscopy, as well as Dr. Harshad Kulkarni and Karla Torres for their assistance with fluorometry analyses.

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547

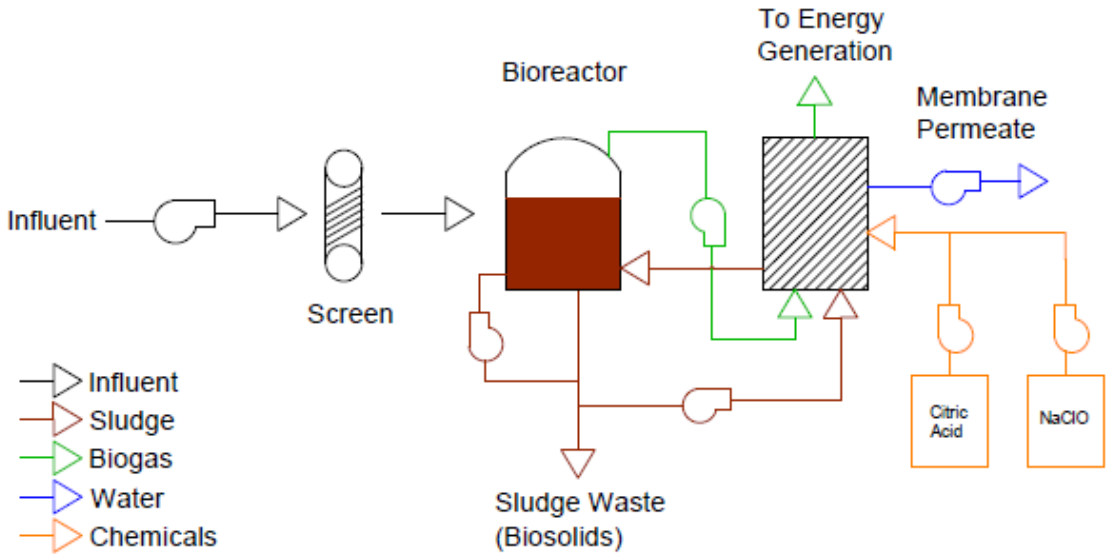


Figure 1. Zoomed in schematic on the bioreactor and the membrane tank. The membrane cleaning sequence is clearly elucidated as shown by the chemical addition to the membrane module section only.

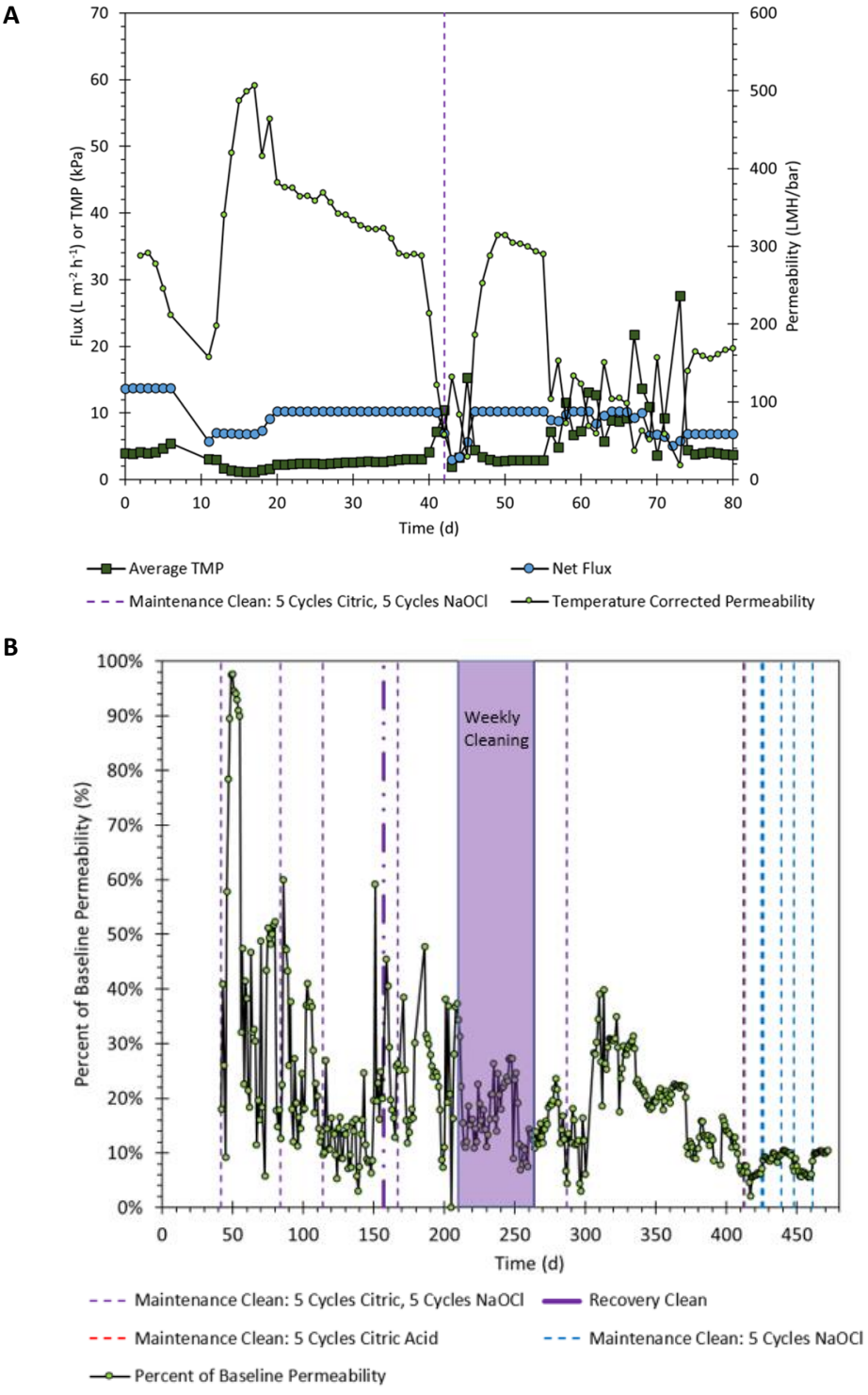


Figure 2. Plots of membrane performance. Figure 2A shows the TMP, Flux, and Permeability over the first 55 days. The first 42 days were operated without chemical cleaning and is used as a benchmark for the system's original permeability. Figure 2B plots the percentage of the benchmark permeability from the first 42 days, and chemical cleaning events.

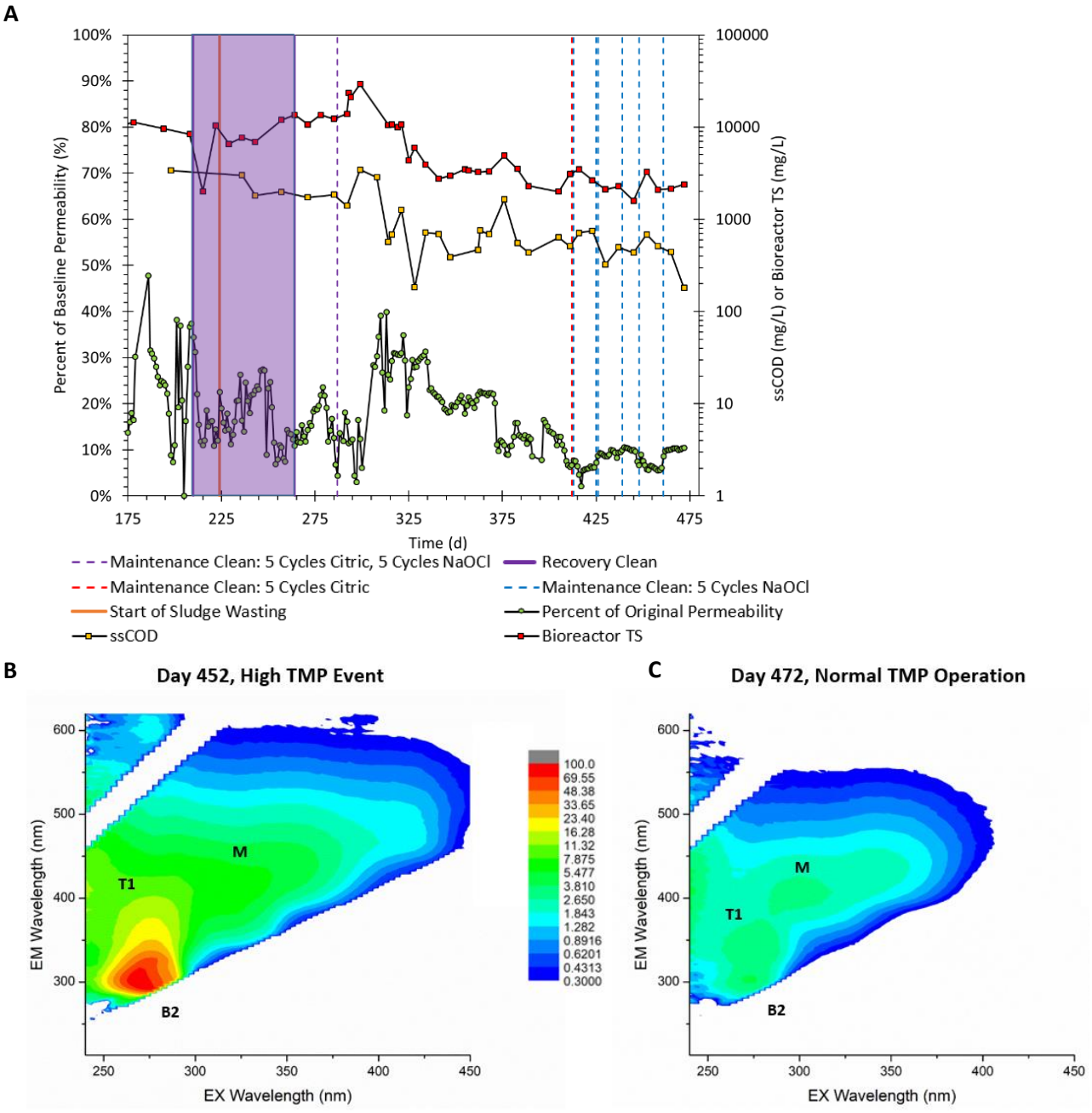


Figure 3. A period of operation from day 175 to the end of operation on day 472 is shown in (A) to show the effects of wasting solids, which affects concentrations of the bioreactor's total solids as well as the bioreactor's semi-soluble chemical oxygen demand (ssCOD), on permeability. (B) and (C) are Excitation-Emission Matrices (EEMs) generated from fluorometer data, which are used to further characterize the soluble organic matter in the membrane permeate during a high transmembrane pressure (TMP) event (44 kPa) and during normal TMP conditions (<30 kPa). During high TMP conditions (B) fluorophore B2, indicative of tyrosine-like compounds, is predominant, but the impacts of a tryptophan-like peak (T1) and a humic-like peak (M) are apparent. B2 is present during lower TMP operation (C) at lower concentrations, and the T1 and M peaks are more clearly identifiable.

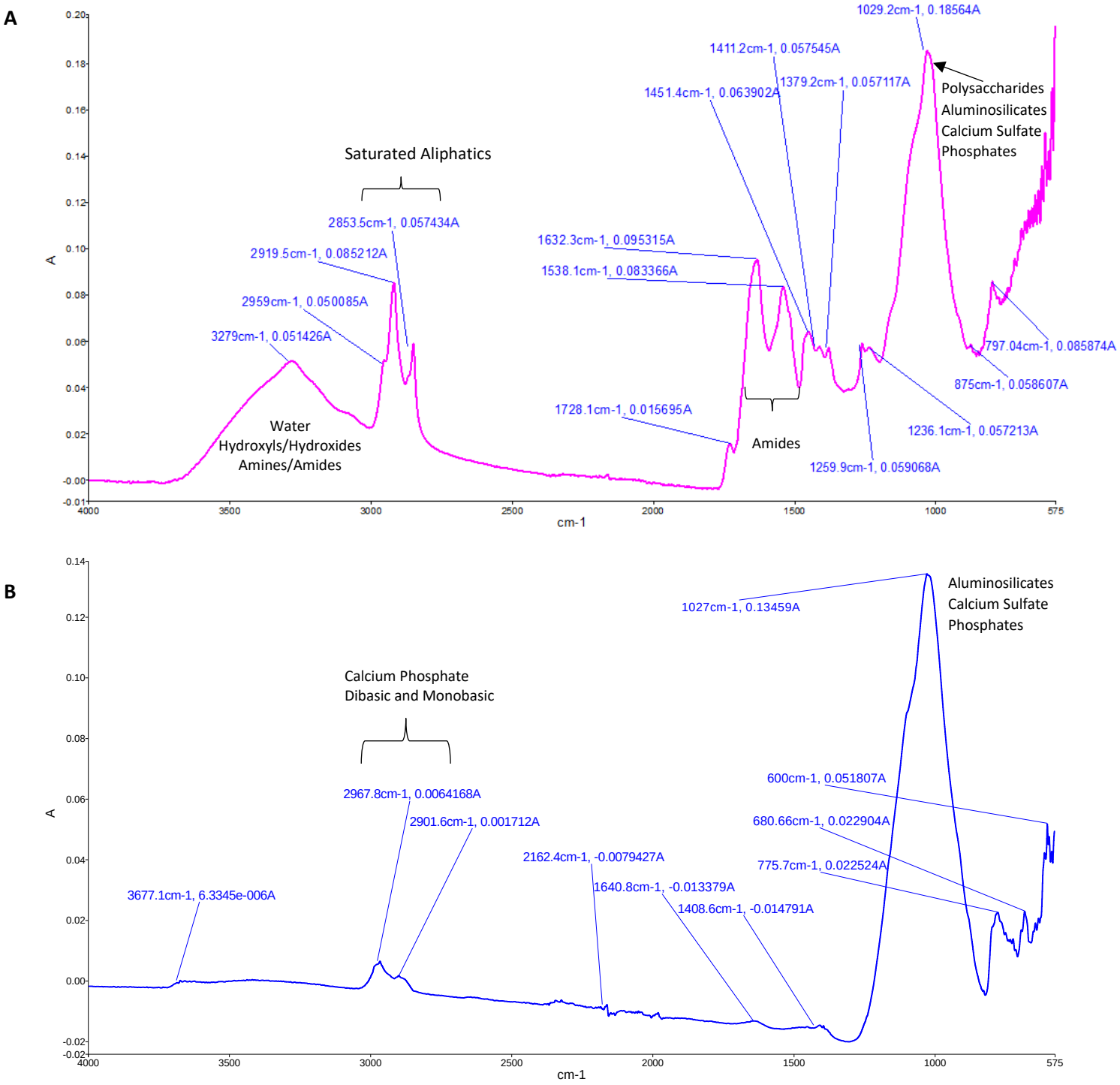
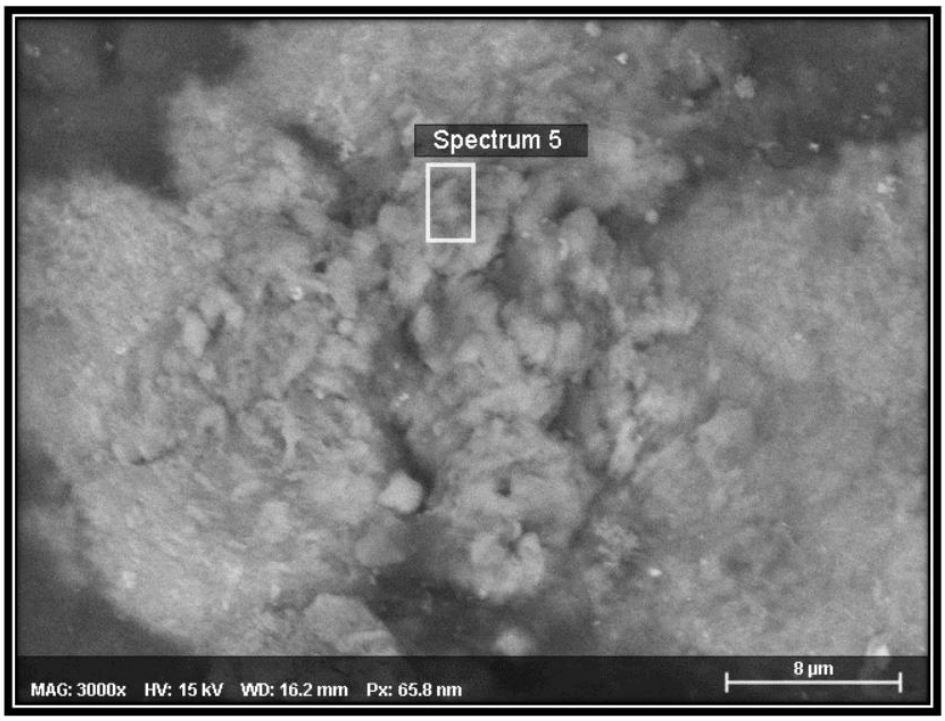


Figure 4. Fourier Transform Infrared (FTIR) Spectroscopy Spectra of dehydrated foulant from the cake layer (A) and foulant after ignition at 450ºC for 8 hours to combust the organic materials present and leave only inorganics (B).

A



Spectrum 5

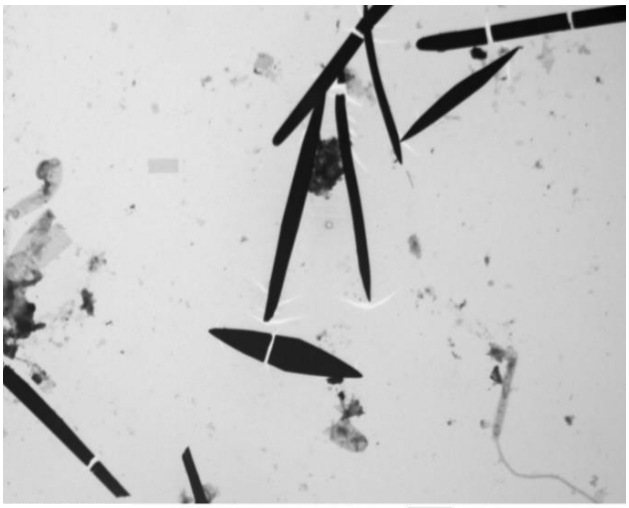
Element	Atom [%]
Fluorine	10.89
Silicon	0.36
Phosphorus	0.21
Sulfur	5.24
Calcium	5.49
Iron	0.32
Sodium	0.39
Aluminium	0.24
Potassium	0.11
Nitrogen	6.67
Carbon	40.46
Oxygen	29.61
	100.00

Carbon, Nitrogen and Oxygen Ignored

Spectrum 5

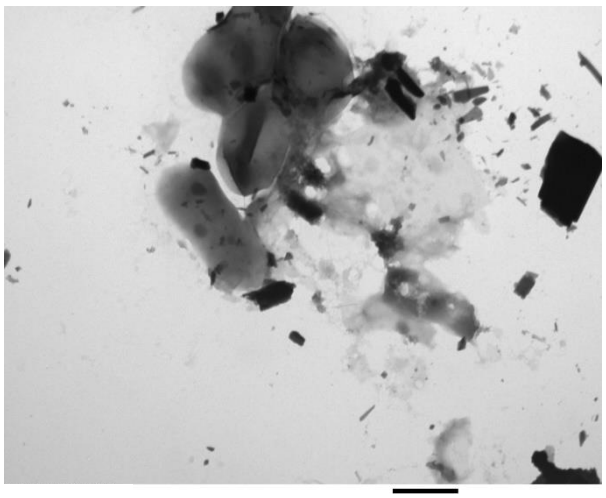
Element	Atom [%]
Fluorine	39.30
Silicon	1.76
Phosphorus	1.01
Sulfur	25.33
Calcium	27.29
Iron	1.69
Sodium	1.92
Aluminium	1.18
Potassium	0.52
	100.00

B



TEM Mode: Imaging
2 µm
Direct Mag: 2600x

C



TEM Mode: Imaging
600 nm
Direct Mag: 13500x

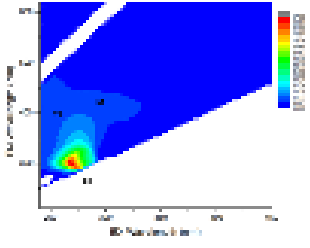
Figure 5. Representative micrographs and microscopy results. (A) shows a representative scanning electron microscope image and its accompanying EDX table for spectrum 5. (B) and (C) are transmission electron microscope images of inorganic crystalline calcium sulfate, an unexpected inorganic scalant that was encountered throughout the foulant cake layer.

Environmental Science: Water Research & Technology

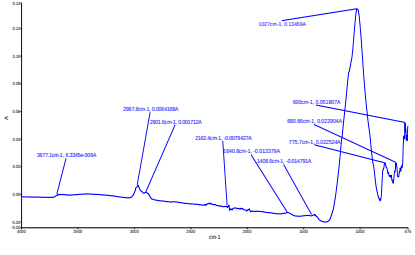
Fouled Membranes

Proactive Monitoring

Fluorometry

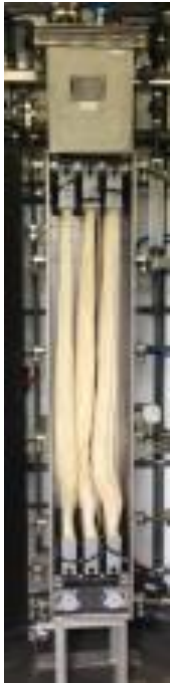


Foulant Characterization



FTIR

Improved Membrane Maintenance



Clean Membranes