Flux recovery of a forward osmosis membrane after a fouling process

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Wastewater treatment through forward osmosis (FO) membranes is a process that has been evaluated in the past years as an innovative technology for the Next Generation Life Support Systems. FO technologies are cost effective, and require very low energy consumption, but are subject to membrane fouling. Membrane fouling occurs when unwanted materials accumulate on the active side of the membrane during the wastewater treatment process, which leads to a decrease in membrane flux rate. The aim of this study is to identify the materials that cause flux rate reduction due to membrane fouling, as well as to evaluate the flux rate recovery after membrane treatment using commercially available antifoulants. Fourier Transform Infrared (FTIR) spectrometry results identified possible compounds that cause membrane fouling and FO testing results demonstrated flux rate recovery after membrane treatment using antifoulants.

Nomenclature

AFM = Atomic Force Microscopy
ARC = Ames Research Center
FO = Forward osmosis
FR = Flux rate
FTIR = Fourier Transform Infrared
JSC = Johnson Space Center

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MF = Membrane fouling
OA = Osmotic agent
SEM = Scanning Electron Microscopy

I. Introduction

IT is impractical to bring the amount of water necessary to supply the crew's needs during a long duration human space flight mission. Hence, there is a need for research and development of lightweight water recycling systems that will provide the astronauts the water supply needed for the duration of the mission. . One such technology is the Forward Osmosis Secondary Treatment system (FOST). FOST has been developed and tested as part of NASA's Next Generation Life Support (NGLS) project [1].

FOST can be used to recycle wastewater, humidity condensate and urine into drinking water to provide astronauts with a reliable water source. However, membrane fouling is still an issue for long term performance of the system. NASA's recent studies have shown that membrane fouling is the primary failure of the FOST system. The aim of this study is to characterize the compounds responsible for membrane fouling and to evaluate if cleaning the fouled membrane can restore the system's flow rate.

II. Background

A. Forward Osmosis (FO)

Forward osmosis is a physical phenomenon that allows the transport of water across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential (Figure 1). FO is driven by a difference in solute concentrations across the membrane that allows passage of water, but rejects most solute molecules or ions. [2]. In wastewater treatment applications where the solvent is water and the solutes are the contaminants, the semipermeable membrane is designed to maximize the flux of water through the membrane and not the contaminants [3].

The advantages that can be pointed out about FO are that it is a biologically occurring process so the hydraulic pressure is low or non-existent, it has high rejection of a wide range of contaminants, and it may have a lower membrane fouling propensity than pressure-driven membrane processes.

The general equation to describe water transport in FO is shown as follows:

$$J_w = A(\sigma \Delta\pi - \Delta P)$$

where J_w is the water flux, A is the water permeability constant of the membrane, σ is the reflection coefficient, $\Delta\pi$ represents the osmotic pressure difference across the active layer of the membrane, and ΔP is the applied pressure which is approximately equal to zero [4].
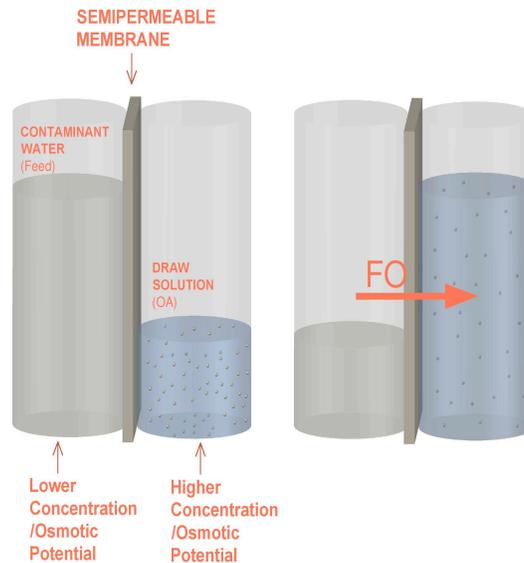
Figure 1. Forward osmosis diagram.

B. Membrane Fouling

Membrane fouling occurs when unwanted material accumulates on the active side of the FO membrane, which eventually leads to a decrease of the water flux across the membrane. The fouling could be reversible if the layer of foulants is formed on top of the membrane (known as cake layer) or irreversible, if the pores of the membrane get blocked by the foulants [5], depending on the chemical and physical properties of the fouling agents . Membrane fouling can be classified in the following cathegories depending on the origin of the materials that precipitate; inorganic fouling, organic fouling and biofouling.

Inorganic fouling is often presented by the term "mineral scaling" because it is mainly due to a presence of inorganic salts in the feed solution that deposit on the membrane. Calcium sulfate ($CaSO_4$), calcium carbonate ($CaCO_3$), silicon dioxide (SiO_2) and barium sulfate ($BaSO_4$) are some of the most common inorganic salts responsible for scaling on the membrane surface. The salt precipitates when the solubility product of the constituent ions is reached or exceeded [6].

The organic fouling of a membrane is caused by a deposition of biopolymers. Previous studies have demonstrated that the major percentage of those polymers are proteins and polysaccharides [7] more specifically polysaccharides and other non-setteable organic matter with a molecular weight larger than 120 000 Da [8]. Biological precipitation can be another contribution to inorganic fouling. The biopolymers contain ionisable groups (COO- , CO32- , SO42- , PO43- and OH-) which are easily capturable by metal ions. Metal ions play a significant role in the formation of fouling layers, which can bridge the deposited cells and biopolymers and then form a dense cake layer. There exists a synergistic interaction among biofouling, organic fouling and inorganic fouling [9].

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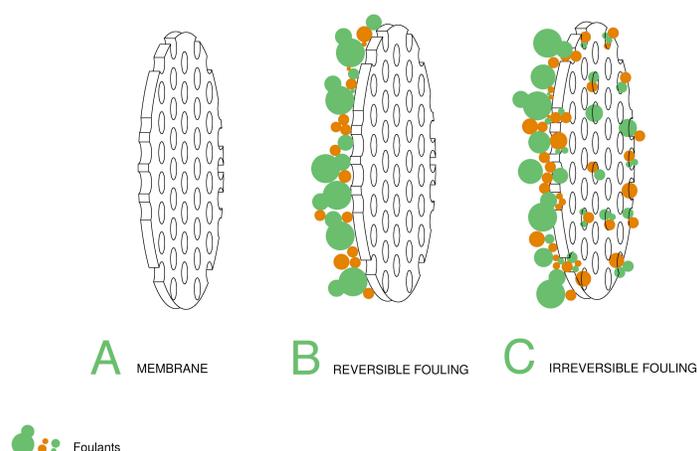
Figure 2. Schematic drawing of reversible and irreversible fouling.

III. Materials and Methods

A. Fouled Membrane

The FOST fouled membrane was acquired after FOST completed a testing program at Johnson Space Center (JSC) as part of the NGLS project. The feed consisted of humidity condensate, hygiene water and urine pretreated in a bioreactor. The chemical composition of the feed solution was analized at the end of each run (feed brine) and as an example, the results of the feed analysis from one of the runs is shown in Table 1. Although the data shown in Table 1 represents only six runs, the feed composition for anions, cations and total organic carbon (TOC) did not vary significantly from run to run. A single flat sheet Porifera Inc. membrane was used to conduct the studies. Porifera Inc., is a company focused on the development of advanced membranes for water treatment, which manufactures high performance FO membranes [10]. The feed was circulated through the FO membrane during 200 hours until the system failed. A decrease in flux rate and the deposition of a brownish agent on the surface of the membrane (Figure 3) indicated membrane fouling. Although the control and fouled membranes have the same surface characteristics, the fouled FO membrane shows a different pattern than the FO control membrane and the reason is that the membrane was placed between spacers during the membrane testing so the membrane coupon acquired the form of the spacer.

The membrane was then brought to NASA Ames Research Center (ARC) to determine the composition of the foulant and to evaluate whether if chemical treatment of the fouled FO membrane using commercially available membrane cleaners could restore its performance.

Table 1. Chemical composition of the feed .

ID	Chloride mg/L	Nitrite mg/L	Nitrate mg/L	Phosphate mg/L	Sulfate mg/L	Sodium mg/L	Ammonia mg/L	Potassium mg/L	Calcium mg/L	Magnesium mg/L	TOC mg/L	TDS mg/L
8/14	12281	113	236	977	3242	8286	2659	1800	542	<0.5	459	28860
8/15	8559	220	273	747	1566	5572	2392	1516	126	<0.5	331	22350
8/21	10468	421	314	987	1608	6672	2550	1929	144	<0.5	386	26290
8/22	11159	549	403	1113	1676	7096	2925	2151	128	<0.5	442	28835
8/23	13285	483	308	1099	1800	8568	2543	2097	122	<0.5	388	30425
8/26	10827	485	309	881	1409	6943	2421	1787	108	<0.5	337	26240
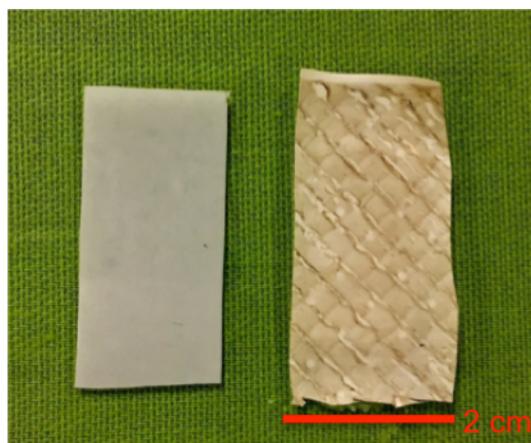
Figure 3. Forward osmosis control membrane (unused) and fouled forward osmosis membrane.

B. Scanning Electron Microscopy (SEM)

Sections of the control and fouled membrane were sputtered with a 5.5 μm layer of gold using a Denton Vacuum HP Cold Sputter/Etch unit. SEM imaging was performed using a S4800 scanning electron microscope (Hitachi, Pleasanton, CA).

C. Atomic Force Microscopy (AFM)

The AFM images were obtained by a NanoScope® V-Multimode 8.15 atomic force microscope from Bruker Corporation with a type E scanner. We performed tapping mode technique using an antimony (n) doped Si cantilever from Bruker AFM Probes, (Camarillo, CA).

D. Fouling Characterization

Samples of the fouling agents were collected using a *Corning® Small Cell Scraper* from the active layer of the previously fouled FO membrane (Figure 3.a). The samples were placed in a weight boat, and dried in a vacuum desiccator for 72 hours. Following the drying process, the fouling agents were subjected to Fourier Transform Infrared (FTIR) spectrometry analysis (Figure 3.b). A representative sample of the dried residue was transferred to an infrared transmitting substrate and examined by the Fourier Transform Infrared Spectrometer (FTIR, Thermo Nicolet 6700) with the FTIR Continuum microscope in transmission mode.

Figure 4. (a) Fouling agents scraped off from the forward osmosis membrane and (b) dried fouling agents.

E. Membrane Performance Testing

The membrane performance testing was conducted on a bench scale system that consisted of two graduated cylinders, each connected to a pump for fluid recirculation purposes (Greylor gear pumps) and two acrylic plates to hold the membrane (Figure 5). The membrane was installed between the acrylic plates and an o-ring that prevented leakage; the active layer of the membrane faced the feed and the membrane support faced the osmotic agent (OA) solution. The test cell had a membrane area of 4.25_X10^{-4} m^2.

Testing was performed using distilled water as the feed solution and a 3.5% sodium chloride (NaCl) solution as the OA. Two tubes were set next to a ruler in order to measure and control the pressure of the fluids. The pressure in the feed side was always higher than in the OA side.The gear pumps were used to generate directional flow on each side of the membrane, both in and out the acrylic plates. After a ten minute stabilization period of the system, measurements of the feed and OA solutions were tracked every hour during a five hour period. For test reproducibility purposes, all tests were conducted in triplicate. First we tested the control FO membrane (brand new membrane that wasn't previously used) and then the fouled FO membrane.
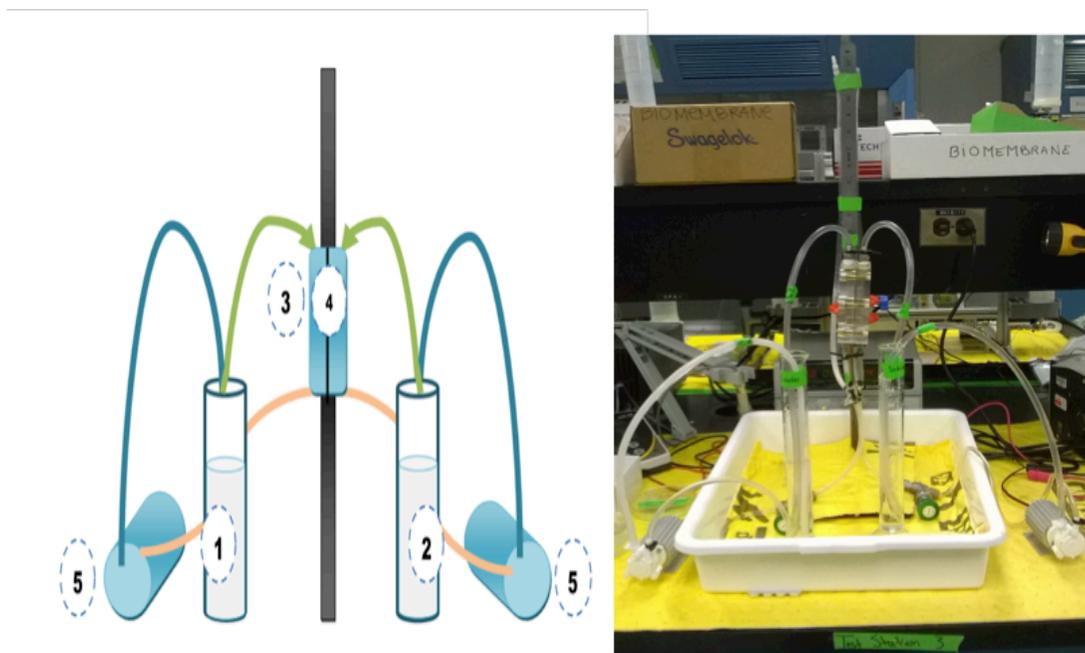
Figure 5. (a) Membrane testing setup diagram and (b) bench scale membrane testing apparatus.

F. Chemical Cleaning

To restore the permeability of the fouled membrane, two different membrane cleaners were used to clean the membrane: King Lee 1000 (hardness scale removal) and King Lee 2000 (organic removal). King Lee technology cleaners is a commercially available cleaning solution that safely removes a wide range of foulants from membrane surfaces.

A 10% antifoulant solution was circulated through the testing cell using the same procedure as mentioned in the membrane performance testing section. After each cleaning process, the membranes were tested using distilled water as feed and a 3.5% NaCl solution as OA respectively, in order to verify any improvement in flux rate.

IV. Results

A. FTIR Analysis

The components from the FO membrane were identified as a biological polyamide such as the protein in skin and/or a synthetic polyamide such as a polymeric resin; inorganic silicate such as silica, and relatively smaller amounts of an ester and possibly aliphatic hydrocarbons.

Figure 4 shows the FTIR spectrum of two micro-pieces of the components from the FO fouled membrane, in an overlay format, demonstrating its homogeneity (i.e., the match of the bands between the two measurements). The components were identified as biological polyamide such as the protein in skin and/or synthetic polyamide such as a

polymeric resin (bands at ~ 3292, 2921, 2851, 1657, 1544, 1463 and 1381 cm-1), inorganic silicate such as silica (bands at ~ 1102 and 805 cm-1), a small amount of ester (weak band at ~ 1734 cm-1), and possibly aliphatic hydrocarbon (intensity of the bands at ~ 2921 and 2851 cm-1).
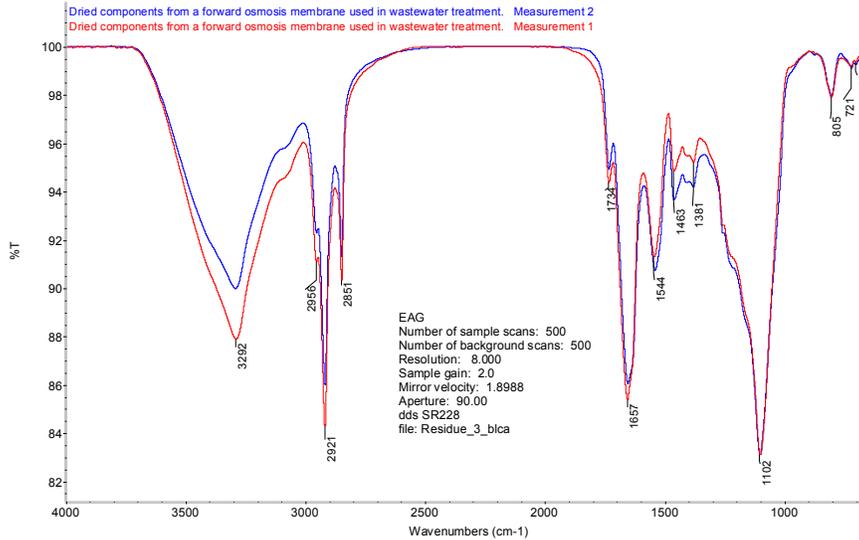

Figure 6. FTIR spectrum of dried components from a forward osmosis membrane used in wastewater treatment.

B. Morphological analysis

The membrane surface was characterized by SEM and AFM. The SEM micrograph of the fouled membrane (Figure 7b) shows a layer formed on the membrane surface due to the accumulation of materials from the feed solution, which consisted of humidity condensate, hygiene water and urine pretreated in a bioreactor. The layer formed on the surface of the membrane masks the structure of the FO membrane, as it prevents the visualization of the pattern of oval structures shown in the control FO membrane (Figure 7a).
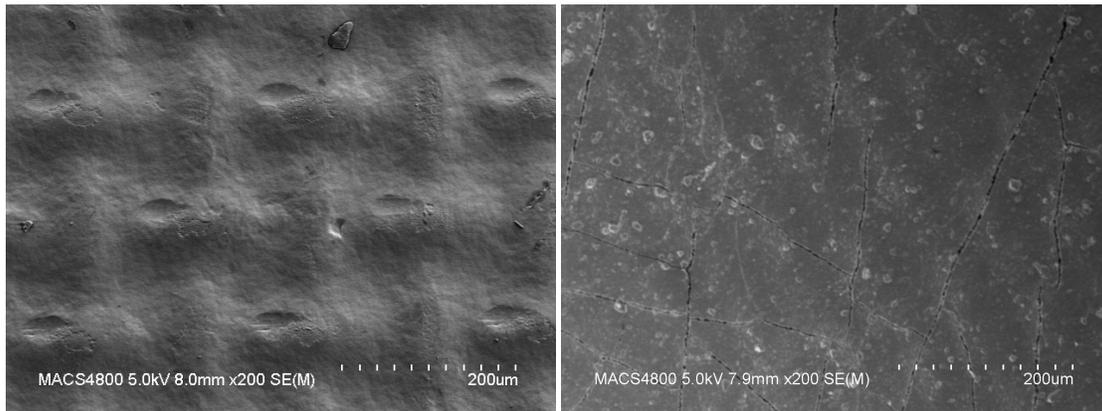

Figure 7. (a) Micrograph of the control forward osmosis membrane and (b) fouled forward osmosis membrane.

The AFM images of the FO control and the fouled membrane show a surface height of 206.7 nm and 929.5 nm respectively (Figure 8). This change in height is due to the accumulation of materials from the feed solution on the surface of the fouled FO membrane. The peaks observed in the FO control membrane image correspond to the nature of the membrane leading us to use the smoothness of the surface as a characteristic to confirm the presence of biopolymers on the surface.
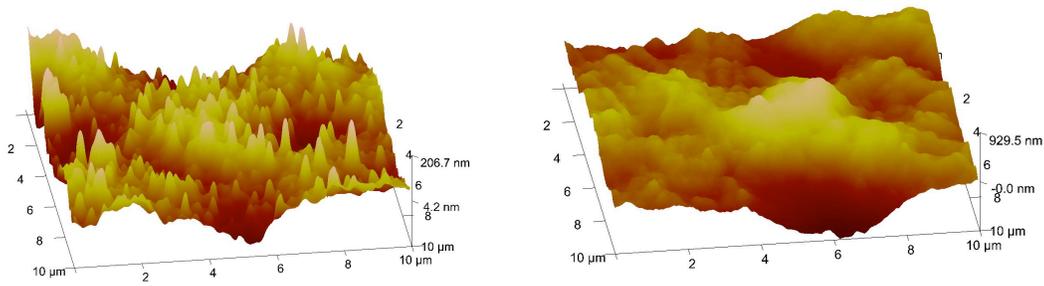

Figure 8. (a) AFM image of forward osmosis control membrane and (b) fouled forward osmosis membrane.

C. Membrane performance testing

Figure 9 presents the difference flow rates obtained during the five hours runs testing the control FO membrane in comparison to the fouled FO membrane. The control FO membrane reached a higher flow rate (96 ml) after a five hour run, while the fouled membrane reached a lower flow (88 ml) after the membrane testing with the same time of duration.
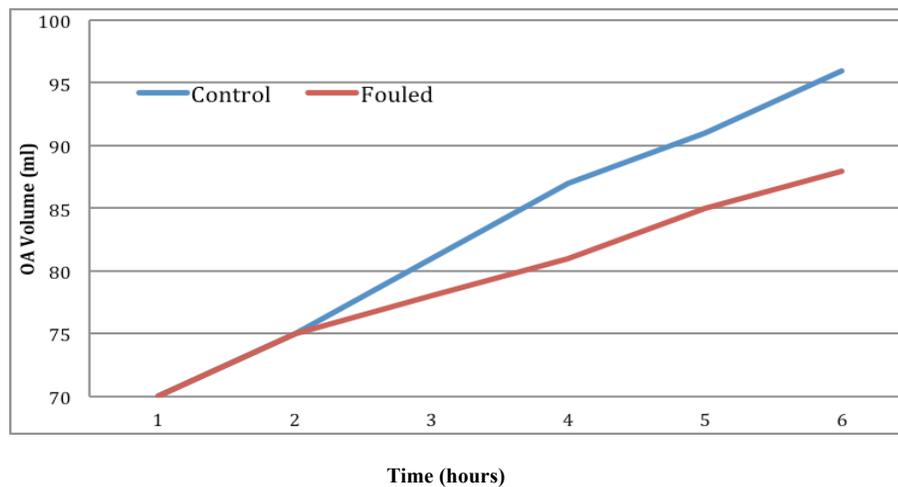
Figure 9. Flow of the fouled and control forward osmosis membrane.

Figure 10 shows the flow rates obtained after membrane testing of the control FO membrane and the fouled FO membrane in comparison to the flux rates obtained from testing the fouled FO membrane after exposure to two different cleaners. The data obtained for the control and fouled FO membrane are the values shown in the previos image. The flow rate after membrane cleaning with one of the cleaners, KL1000 (hardness scale removal) are

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similar to the flux rate obtained during membrane performance testing of the fouled membrane. After cleaning the membrane with KL2000 (organic removal) there is an improvement of the flux rate of about 31% after the membrane performance testing was conducted. However, even if the fouled membrane was treated with the different cleaners ,the flow rate did not recover the flux rate obtained during the FO control membrane testing.
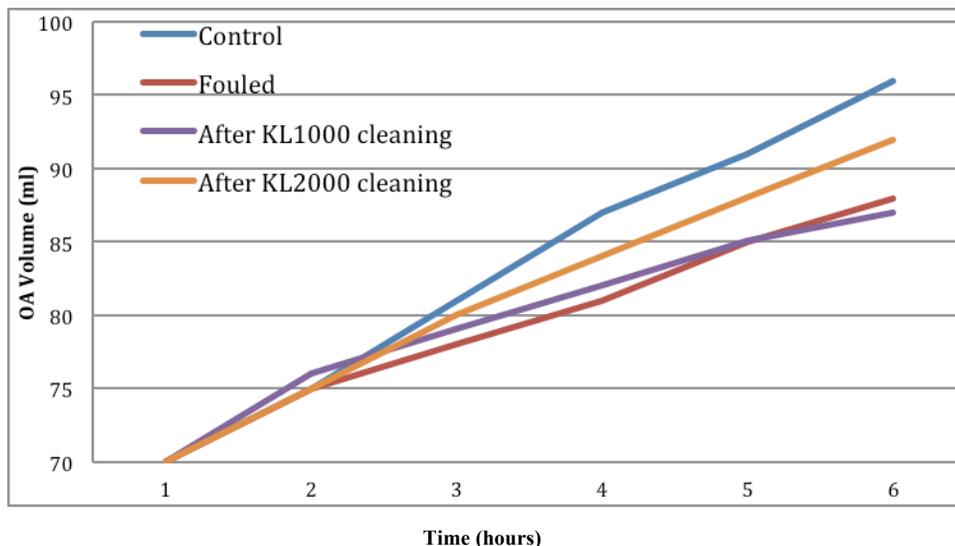

Figure 10. Flow of control, fouled FO membranes and FO membranes after cleaning procedures.

V. Conclusions

The materials deposited on the active layer causing membrane fouling were removed and characterized as biological and synthetic polyamide, silica, amounts of an ester and possibly aliphatic hydrocarbons. The characterization of these materials will be useful to develop techniques specific to prevent the accumulation of organic mateiales in the active layer of the membrane and to look for new cleaning products suitable for the targeted molecules.

Eventhough there was an improvement in the flow rate obtained after the membrane cleaning using the different products, the original performance was not completely restored. The flow rate obtained for the control membrane increased in 37%, while the flow rate obtained after usage of the KL1000 cleaner was improved by 24%, and after the KL2000 cleaner the flow rate increased 31%. Membrane fouling is a phenomenon that could be mitigated by finding the appropriate cleaners, and that will depend on the composition of the feed and the materials that accumulate on the active layer of the membrane.

Acknowledgments

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