The effect of fatty acids to protect forward osmosis membranes from damage

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NASA has conducted research and development on forward osmosis (FO) membranes for wastewater reclamation in space since 1993. The lessons learned during operation of the International Space Station and FO based technologies on the ground taught us that reliability is a key limitation. Membranes are susceptible to organic fouling, oxidation and calcium scaling, and these factors tend to damage the membrane reducing their operating life and performance. The development of a Synthetic Biological Membrane (SBM), a membrane that mimics naturally occurring biological processes, will mitigate membrane damage and improve reliability. The SBM is a lipid-based membrane with a protective fatty acid layer configured for use in a FO water purification system. In this configuration, the protective layer on the surface of the lipid membrane is composed of fatty acids (FA). The FA interact with the chemicals found in the wastewater feed, and protect the membrane from damage. In this study, we conducted preliminary experiments to determine the feasibility of using fatty acids to alleviate damage from calcium scaling, oxidation and organic fouling.

Nomenclature

CMC	=	critical micelle concentration
EPA	=	Environmental Protection Agency
ESI	=	Early Stage Innovation
FO	=	forward osmosis
FA	=	fatty acid
ISS	=	International Space Station
LM	=	lipid membrane
NASA	=	National Aeronautics and Space Administration
OA	=	osmotic agent
ppm	=	parts per million
RO	=	reverse osmosis

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SBM = synthetic biological membrane
TOC = total organic carbon
TDS = total dissolved solids
TSS = total suspended solids
WR = wastewater reclamation

I. Introduction

CURRENTLY available commercial membranes have short life spans. This is due to membrane susceptibility to organic and inorganic fouling, which leads to a reduction in membrane performance. To alleviate these problems, National Aeronautics and Space Administration (NASA) has conducted research on a novel biomimetic material for wastewater recycling applications based on forward osmosis (FO) membranes. The Synthetic Biological Membrane (SBM) is a new generation of FO membranes, that mimic naturally occurring biological membranes [1].The objective of the SBM is to develop a membrane system with extended life capabilities that are derived from regenerative characteristics of living systems. The goal of the SBM is to use it in a bioregenerative life support system suitable for a long-term crewed mission to the Moon or Mars.

The SBM will be integrated into a FO water recycling system to demonstrate its functionality regarding wastewater treatment applications. FO membranes are semipermeable membranes able to separate two fluids of different solute concentrations. The FO process is driven by the osmotic potential difference between the two solutions [2]. The membrane allows the solvent to pass through it but rejects the solutes. The flux of solvent across the membrane continues until the osmotic potential across the membrane is equalized and the solute/solvent concentration on both sides of the membrane is in equilibrium. In wastewater treatment applications the feed crosses the semipermeable membrane into the osmotic agent (OA) side (solution with osmotic pressure higher than that on the feed) and the membrane is designed to maximize the flux of water through the membrane while rejecting the contaminants and minimize salt back flux.

To develop the SBM, synthetic biology techniques will be used to genetically engineer organisms that will hyper-express fatty acids that provide a protective layer to the active side of the lipid membrane. The lipid membrane is a semipermeable membrane made of two layers of phospholipids, just like cell membranes. The genetically engineered organisms will be grown in the OA solution where they continuously produce fatty acids (FA). The lipid membrane will be engineered to be permeable to FA, that will be transported across the membrane. The driving force is the concentration gradient [3]. Once on the feed side of the membrane the fatty acids will either precipitate from solution and adhere to the membrane creating a protective layer, or they will react with contaminants in the solute layer that builds up adjacent to the feed side of the membrane. This process along with continuous replacement provides a cleaning for the surface of the membrane and a mechanism for biological regeneration of damage.

The SBM is a NASA Early Stage Innovation (ESI) project. ESI has supported extensive experimental work conducted in different areas during the past couple of years. The aim of this study is to identify suitable fatty acids and to conduct preliminary experiments to determine the feasibility of the selected fatty acids to alleviate damage from calcium scaling, oxidation and organic fouling. Concomitantly, membrane permeation experiments were conducted to test whether if the selected FA would be able to permeate across the biomimetic membrane.

II. Background

A. Membrane damage and fatty acids

The accumulation of unwanted materials on the surface of a membrane is known as “fouling”, which eventually will lead to membrane failure. There are different types of membrane fouling based on the composition of the materials (organic and inorganic compounds). Previous studies have shown that the organic fouling of a membrane is caused by a deposition of biopolymers, specifically polysaccharides and other non-setteable organic matter with a molecular weight larger than 120 000 Da, and biological precipitation [4]. Inorganic fouling is also known as calcium scaling which is caused by pH dependent precipitation of calcium and other divalent cations like carbonate salts [5]. The biomembrane may become oxidized/damaged by reactive oxygen species (hydroxyl radicals, superoxide anions,

and hypochlorite anions) that cause lipid "peroxidation." This results in a lipid radical, followed by the formation of a lipid with an attached peroxy group.

The purpose of using FA is to remove contaminants that are responsible for fouling the lipid biomembrane. Fouling resulting from calcium scaling, organic deposition and oxidation damage. FA are carboxylic acids with a long aliphatic chain that play essential roles in living entities as signal molecules, energy depositories and basic units of cell membranes. Since FA are produced extracellularly by different types of microorganisms, there is no need for cell lysis [6,7]. Medium and long chain FA have higher critical micelle concentrations (CMC), thus in water they would form cristallyne and liquid-cristallyne aggregates which can be used directly without any processing to disrupt micelles [8]. The lipophilic character of FAs gives them the ability to directly diffuse across the plasma membrane [9]. The characteristics mentioned above make FA ideal candidates for integration into the SBM system.

Extensive literature research was done and FA interaction with calcium and other potential fouling substances, culled the initial list of fourteen potential candidates down to nine FA, and provided justification for our selections[10]. The FA candidates were selected based on the ability to change calcium solubility based on acidity, to bind to the biomembrane, to mitigate organic fouling by partitioning organics into vacuoles, to protect against oxidation through oxidation reaction with biocides and hydroxyl ions, to diffuse into and across the biomembrane, the high production yelds by microbial systems and the FA availability through genetically engineered microorganisms.

Based on the considerations provided above, the selected FA candidates to be implemented in the SBM are palmitic acid (16C, saturated), myristic acid (14C, saturated), lauric acid (12C, saturated), oleic acid (18C, unsaturated), linoleic acid (18C, unsaturated), alpha-linoleic acid (18C, unsaturated), hexanoic acid (6C, saturated), decanoic acid (10C, saturated) and octanoic acid (8C, saturated).

B. The effect of fatty acids in calcium solubility, oxidation and organic fouling

Calcium deposition on the surface of FO membranes is one of the causes of membrane fouling [11]. Membrane fouling by calcium scaling reduces the flux of the membrane, requires more energy for operation, and requires the use of cleaning agents to remove calcium from the membrane. To alleviate the damage from calcium scaling, the SBM will incorporate a protective layer of specific fatty acids (hexanoic acid, decanoic acid and octanoic acid), that ideally will prevent calcium scaling on the membrane. In this study, preliminary experiments will determine the feasibility of using fatty acids to control calcium scaling on membranes, by quantifying how fatty acids impact the solubility of calcium.

Organic precipitants have been shown to be the primary foulants of membrane systems when treating human wastes. Previous experimental work on membrane fouling has identified the classes of organic contaminates that are responsible for FO membranes using urine as feed. Among the compunds found is biological polyamide, such as the protein in skin [4]. Due to inaccesibility to obtain biological polyamide, albumin was selected as an organic simulant for these compounds. This testing will evaluate the ability of fatty acid micelles (palmitic acid, myristic acid, lauric acid) to encapsulate organics and to remove them from solution [12].

Both galactic and solar radiation can produce hydroxide radicals in water solutions. These radicals can produce oxidation damage on membranes. In addition, in order to test the SBM on the International Space Station (ISS), the SBM should be resistant to oxidative damage from chromic acid (hexavalent chromium) which is used as a urine pretreatment on board ISS. Therefore, oxidation damage protection is a required characteristic of the biomembrane. To alleviate membrane damage from oxidation, the SBM will incorporate a protective layer of FA (oleic acid and linoleic acid) that will serve as a sacrificial layer protecting the membrane. This work, will conduct preliminary experiments using sodium hypochlorite as an oxidant agent to determine the feasibility of the FA to mitigate the damage.

III. Experimental Protocol

A. Testing the effect of fatty acids in calcium solubility

Hexanoic acid has been the selected FA to control calcium scaling in this study. Hexanoic acid (153745 Sigma-Aldrich) was added to a calcium carbonate solution at ranging concentrations; 0% (control), 1%, 5%, 10%, and 20%. The calcium carbonate solution was prepared by mixing 10 mL of 1M of calcium chloride (223506 Sigma-Aldrich; prepared by dissolving in deionized water and then filtered through a 0.20 um filter) and 10 mL of 1M sodium carbonate (S7795 Sigma-Aldrich; prepared by dissolving in deionized water and then filtered through a 0.20 um filter). The pH was measured before and after the addition of the different hexanoic acid solutions into the calcium carbonate solution. Additionally, samples of each solution were removed and analysed for total suspended solids (TSS) and total dissolved solids (TDS) using the following methods; EPA method 160.2, Gravimetric, Dried at 103-105Ec and EPA method 160.1. For reproducibility purposes, experiments were conducted in triplicate for each concentration of hexanoic acid.

B. Oxidation studies

For the oxidation assay, the targeted FA was oleic acid and sodium hypochlorite as the oxidant. A solution containing 65 mg of sodium hypochlorite in 1L of distilled water was prepared . The pH and oxidation reduction potential values of the sodium hypochlorite solution were recorded. Oleic acid (2000 mg) was added to the sodium hydroxide solution and pH and oxidation reduction potential values measured every 24 hours for 11 days. Four different experiments were conducted were oleic acid was added to the sodium hydroxide solution and only two runs where the FA wasn't added to the sodium hydroxide solution.

C. Organic fouling

The selected fatty acid to conduct preliminary studies on organic fouling mitigation was oleic acid and lauric acid. Reagent grade albumin was used to prepare two different solutions (500 ppm) 100 mg of oleic acid were added to one solution and 100 mg of lauric acid to the other solution. The solutions were set at room temperature for 24 hours. After 24 hours, samples from both solutions were collected and analyzed for total organic carbon (TOC). Different samples from both solutions (albumin and oleic acid solution, albumin and lauric acid solution) were collected and filtered through a 0.15 micron filter and analyzed for TOC. For test reproducibility, experiments were performed in triplicate for oleic acid and lauric acid.

D. FA permeability studies

Additonal testing was conducted to see if the FA would permeate through the membrane. Myristic acid, decanoic acid and oleic acid were the selected FA to perform permeability studies across the FO membranes. Preliminary studies on FA solubility conducted at NASA Ames have shown that these 3 FA seem to have higher solubility in water in comparison to the rest of the FA potential candidates proposed for the SBM.

The fatty acid permeation rate experiments were performed using two different membranes. The two types of membranes appear to have similar material characteristics but their specific composition are proprietary of the membrane manufacturers so that information will not be provided on this manuscript. In this paper, these two membranes will be referred to as FO1 and FO2. Both membranes are tested in flat sheet contactors.

FA solutions were made by adding a single FA (~100 ppm) at a time to a fixed volume of distilled water and raising the pH to 12.0 using reagent grade sodium hydroxide. The pH of 12.0 was maintained during this experiment because it improves the solubility of FA in water. The solution was run on one side of the membrane with a pH 12.0 water solution flowing on the other side of the membrane. Liquid samples were taken before and after 1 hour of recirculating the solutions across the membrane and analyzed for TOC. The TOC is proportional to the fatty acid concentration on both sides of the membrane, which is used to calculate the permeation of each specific FA.

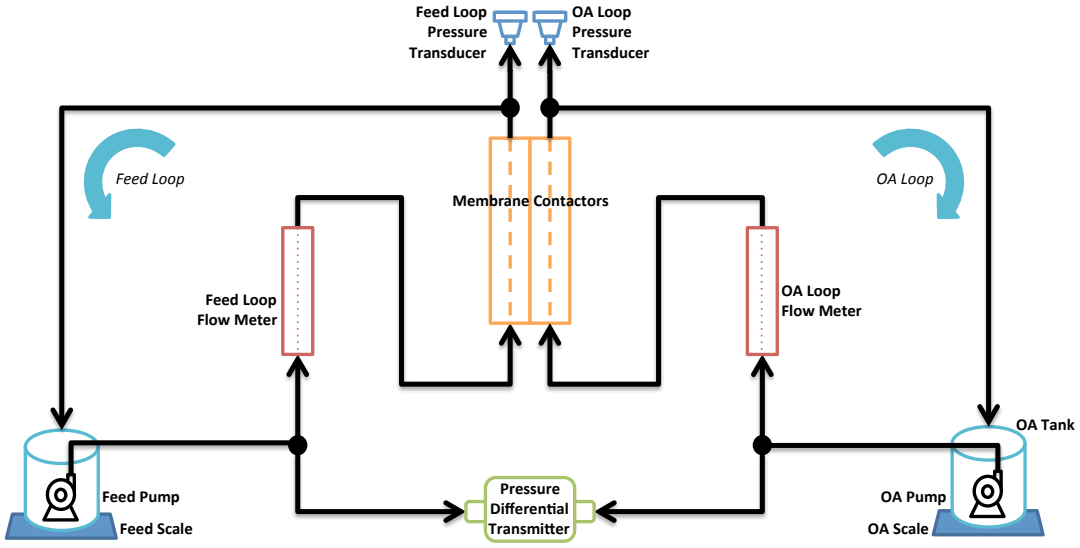

Figure 1. Membrane testing diagram. The membrane is placed between the membrane contactors for FA permeability studies.

IV. Results

A. The effect of FA on calcium solubility

TSS is a measurement for non-ionic solids. This measurement is used to quantify insoluble solids. Therefore this value is used to quantify insoluble calcium. Instead, TDS is used to quantify the amount of ions dissolved in the solution, in other words the amount of calcium that is solubilized. Table 1 shows the average and standard deviation values for TDS and TSS obtained after adding different concentrations of hexanoic acid (1% and 5%) in the calcium carbonate solution. The corresponding values for 10%, and 20% of hexanoic acid are not shown in this table due to a high scatter in the data, probably from the interference of the analytical instrumentation and the suspended solids (Figure 2). The pH was also measured as different concentrations of hexanoic acid were added to the calcium carbonate solution (Figure 3).

Table 1. Average and standard deviation values for TDS and TSS

% Hexanoic Acid	Average % TDS	Average %TSS
0	5.8 ± 0.0	3.8 ± 0.5
1	8.0 ± 0.1	2.5 ± 0.1
5	7.0 ± 0.1	1.7 ± 0.1

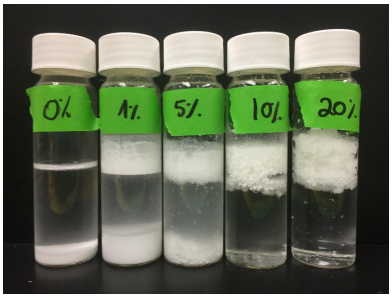

Figure 2. An image showing the effect of FAs on calcium solubility in 0%, 1%, 5%, 10% and 20% Hexanoic Acid..

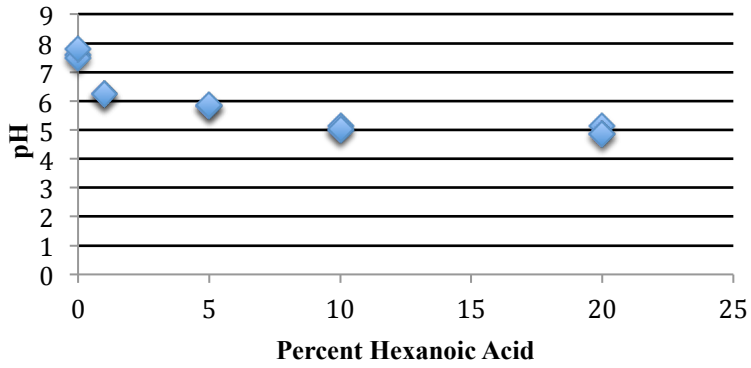

Figure 3.The graph showing the pH of calcium carbonate solution after the addition of hexanoic acid at different concentrations.

B. The effect of FA on membrane oxidation

The results obtained from the oxidation assay are shown in Figure 4. Hypochlorite #1 and Hypochlorite #2 display the oxidation reduction potential (mV) during 11 days of the sodium hypochlorite solution without the addition of the FA. The data for Oleic #1, Oleic #2, Oleic #3 and Oleic #4 show the oxidation reduction potential (mV) over 11 days where oleic acid was added to the hypochlorite solution for the 4 different experiments.

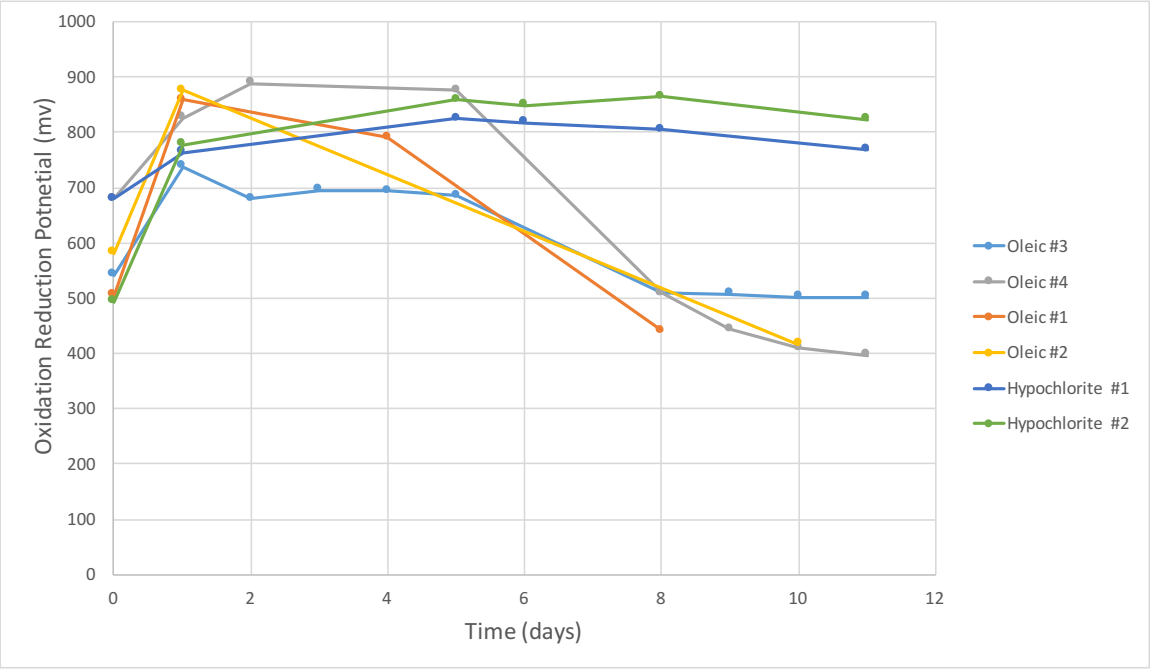

Figure 2. The graph of the oxidation reduction potential (mV) versus run time (days).

C. The effect of FA in organic fouling

The results of the preliminary organic tests are displayed in Figure 5. Addition of oleic acid and lauric acid to a solution containing a high concentration of albumin (organic foulant) resulted in the partitioning of the albumin into micelles created by the fatty acids. The resulting solution was filtered through a 0.015 micron filter to remove the micelles and albumin from the product.

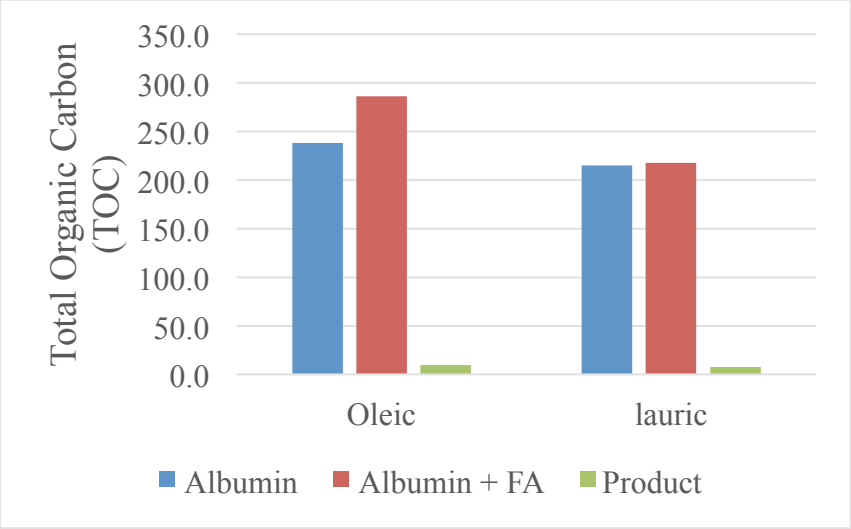

Figure 3. Total organic carbon (ppm) of preliminary testing using oleic acid and lauric acid.

D. FA permeation studies

All the selected FA for the permeability studies were able to permeate across the two different membranes. However, myristic and decanoic acid had similar permeation rates (mol/m^2/hr) on the FO1 membrane and the permeation of the myristic acid seems to be higher across the FO2 membrane. Oleic acid instead, had a significantly lower permeation than the decanoic and the myristic acid but the permeability is similar across both FO1 and FO2 membranes. This could be attributed to the larger carbon chain of oleic acid compared to decanoic and myristic acid, which both have a smaller carbon chain.

Table 2. Results of the different FA permeations across FO1 and FO2 membranes.

Permeation of FA across FO1 membrane		**Permeation of FA across FO2 membrane**	
Oleic acid	0.00162 mol/hr/m^2	Oleic acid	0.00018mol/hr/m^2
Myristic acid	0.00273 mol/hr/m^2	Myristic acid	0.00055mol/hr/m^2
Decanoic acid	0.00272mol/hr/m^2	Decanoic acid	0.00027mol/hr/m^2

V. Conclusion

The mechanisms by which fatty acids mitigate protein fouling is still unknown. There is also much we don't know about how fatty acids prevent membrane oxidation. Further studies are needed to determine the interaction between FA and membrane fouling. However, based on the results of this study, TDS and TSS values demonstrate that the increased solubility of calcium carbonate is due to the addition of hexanoic acid. Oleic acid seems to have an impact in oxidation because the oxidation reduction potential of the sodium hypochlorite remains constant over the time (Hypochlorite #1 and Hypochlorite #2) whereas the oxidation reduction potential of the sodium hypochlorite solution is reduced when the FA is added. Oleic acid appears to have a higher impact on the encapsulation of organic foulants (albumin) than the lauric acid.

Aditionally, genetically engineered organisms tend to produce a pool of FA rather than producing a single fatty acid, so further research would need to be conducted on how a mixture of different fatty acids may impact fouling. Overall, preliminary data from this study shows that the targeted fatty acids for the experiments mentioned above are suitable for mitigation purposes caused by inorganic, organic and oxidation compounds that generate membrane damage.

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