The Use of Porifera Membranes for Urea Rejection in Forward Osmosis Systems

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Forward Osmosis (FO) systems are used to produce clean water from wastewater due to an osmotic pressure difference across a semipermeable membrane. While it is important to have membranes that can produce high water flux and low salt back flux, it is also necessary for them to highly reject organic and inorganic contaminants present in wastewater. It is of our interest to evaluate membranes that can highly reject urea, the main component in urine, without fouling. Currently, there are no commercially available FO membranes that can reject urea. Porifera, Inc. manufactures high performance FO membranes with open-pore hydrophilic configuration with an excellent rejection layer. Porifera FO membranes have three times higher flux and more than three times lower salt passage than conventional cellulose acetate FO membranes. In this work, deionized (DI) water with urea at ppm level was used as feed, while calcium nitrate ($Ca(NO_3)_2$) at a concentration range of 5% to 15% w/w was used as draw solution. The performance of Porifera FO membranes was evaluated terms of water flux rates, salt back flux and urea rejection. Results confirm that Porifera FO membranes have high urea rejection and very low salt back flux.

Nomenclature

DI	=	Deionized water
FO	=	Forward Osmosis
UPA	=	Urine Processor Assembly
w/w	=	Weight by Weight
DS	=	Draw Solution
ISS	=	International Space Station
TOC	=	Total Organic Carbon
LMH	=	Liter per Meter^2 per Hour
ppm	=	Parts per million

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I. Introduction

In recent years, special attention has been paid to Forward Osmosis (FO) systems as a spacecraft water recycling systems. The process of osmosis is described by the net movement of water through a selectively permeable membrane caused by a difference in osmotic pressure across the membrane. FO systems are used to produce clean water from wastewater, gray water and urine using the osmosis principle. While it is important to have selectively permeable membranes that can produce high water flux and low salt back flux, it is also necessary for them to highly reject organic and inorganic contaminants present in wastewater, gray water and specially, urine.

Urine is composed of electrolytes, nitrogenous compounds, vitamins, hormones, organic acids and other organic compounds.[1] Urea (CH_4ON_2, 60.1g/mol), a nitrogen-containing organic compound is one of the main components in urine (36.2%).[2] For this reason, it is of our interest to evaluate membranes that can highly reject urea. Currently, there are no commercially available FO membranes that can effectively reject urea. Porifera, Inc., a company dedicated to develop advanced membranes for water treatment, manufactures high performance FO membranes with open-pore hydrophilic configuration. Porifera FO membranes have three times higher flux and more than three times lower salt passage than conventional cellulose acetate FO membranes.

In this paper we report the study of the performance of Porifera FO membranes in terms of water flux rates, salt back flux and urea rejection.

II. Experimental Section

A. Test Set-up

A single flat sheet Porifera membrane with an area of 4.25 x 10^{-4} m^2 was installed between two acrylic plates. Included in the installation were two plastic nets that served as spacers and an O-ring, to prevent leakage. The skin (active layer) of the membrane faced the feed and the membrane support faced the draw solution (FO mode). Both the feed and the draw solution tubing were connected in parallel to the Cole Parmer Masterflex c/l dual-channel variable-speed tubing pump to generate directional flow in and out the acrylic plates at 60 rpm. Experimental setup and flow diagram of the setup are shown in Figure 1. Conductivity of the feed and draw solution throughout the duration of each experiment was measured with YSI 3200 bench top conductivity meter.

B. Experimental Conditions

Before and between tests, the system was rinsed with 200 ml of DI water. To evaluate the performance of Porifera membrane in terms of flux and salt back-flux, Di water was used as feed and sodium chloride (NaCl) at 1, 3 and 5% w/w as draw solution.

It is known that NaCl interferes with the determination of TOCs.[3] In order to determine TOC content in the samples, and evaluate the urea rejection of the Porifera membranes, it was necessary to choose a salt for the draw solution that does not interfere with the TOC analyzer. For this, it was decided to use $Ca(NO_3)_2$. It is not only highly soluble in water but it also non-toxic, accessible, and cheap, since it is used as fertilizer. $Ca(NO_3)_2$ has an osmotic pressure that is almost 3 times lower than of that of NaCl.[4] To compensate, relatively higher concentrations of the $Ca(NO_3)_2$ draw solution were used. To test urea rejection, urea in DI water (1000, 3000 or 5000 ppm) was used as feed. Each urea concentration was tested with calcium nitrate ($Ca(NO_3)_2$) at 5, 10 and 15% w/w as draw solution. Each experiment was performed for 60 minutes at room temperature. All test were performed in triplicate.

In order to test the urea rejection of the Porifera membrane for a real life application, it was tested for 90 minutes using raw human urine as feed and 10% w/w ($Ca(NO_3)_2$ as draw solution. Table 1 summarizes the experimental procedure for the urea rejection experiments.

C. Sample Analysis

For sample analysis, 40 ml samples were collected in vials from both the initial feed and the initial draw solution. Samples were also collected at the end of the 60-minute experiment of both the final feed and final draw solution. These 4 samples of every experiment were then sent to the lab for analysis: the identification of anions and cations (ThermoFisher (Dionex) Ion Chromatograph) and Total Organic Carbon (TOC) (Shimadzu Total Organic Carbon Analyzer).

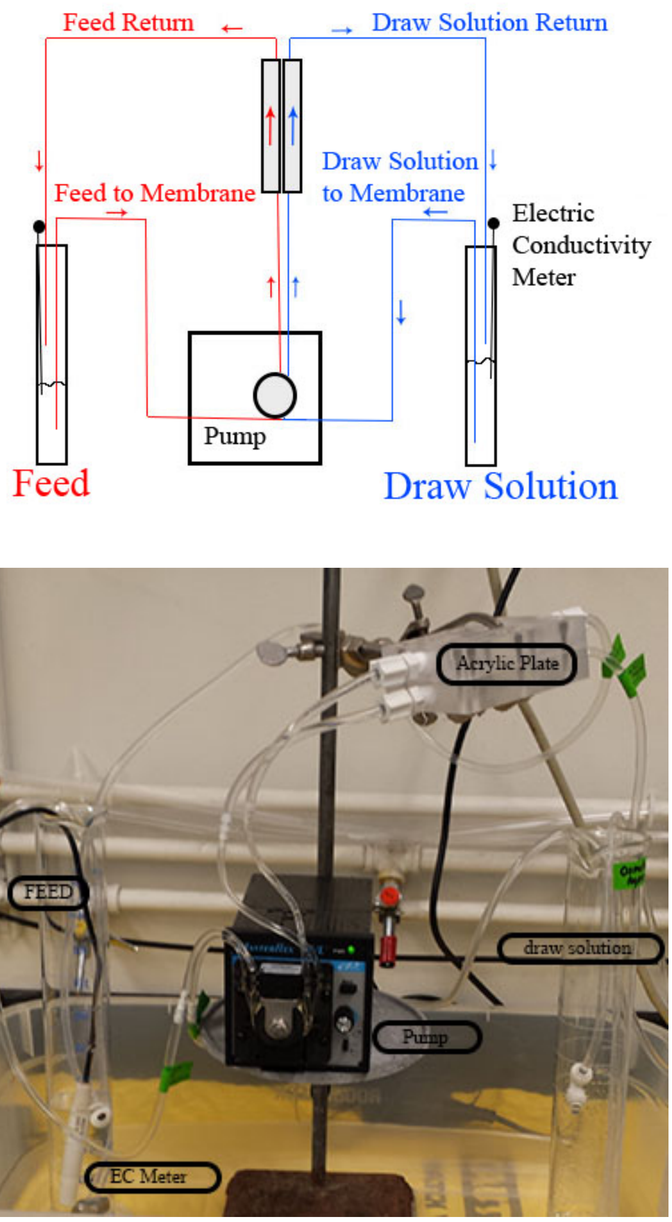

Figure 1: (a) Experimental Setup Diagram showing directional flow of Feed and Draw solution. (b) Photo of the actual experimental set-up.

FEED (urea /DI water) (ppm)	Draw solution($Ca(NO_3)_2$) (%)
1000	5
	10
	15
3000	5
	10
	15
5000	5
	10
	15
urine	10*

Table 1: Summary of the experimental procedure. Each test was performed for 60 minutes and in triplicate. *Tested for 90 minutes.

III. Results and Discussion

In FO systems, the draw solution plays an important role. The ideal draw solution should have higher osmotic pressure than feed and minimal salt-back flux from draw solution to feed, among other characteristics. Draw solutions made with NaCl are often used, not only because the salt meets these criteria but also because of it is non-toxic and is highly soluble in water. The performance of Porifera membrane was evaluated in terms of flux and salt back-flux (ion rejection) when NaCl was used as draw solution. To calculate the water flux rate (J) the following equation was used:

$$J = \frac{(V_f - V_i)_{DS}}{A_{membrane} * t} \quad (1)$$

where, J is the water flux rate (liter per meter^2 per hour (LMH)), V_f is final volume of DS (L), V_i is the initial volume of the DS (L) and t is time (h). $A_{Membrane}$ is active membrane area = 4.25 x 10^{-4} m^2.

Figure 2 shows that the water flux rate linearly increased as a function of the NaCl draw solution concentration. Moreover, Porifera membrane shows to have higher water flux rate at lower NaCl draw solution concentration than a commercially available membrane. For 5% w/w NaCl draw solution, the average flux rate is 19 ± 4 LMH. It has been reported that for a commercial FO membrane the water flux rate is 7.2 LMH when an 11.7% w/w (2 mol/L) NaCl draw solution was used.[5] Table 2 summarizes the results for ion rejection. Porifera membranes reject over 99.9% both Na^+ and Cl^-. Therefore the salt back-flux from draw solution to feed is ≤ 0.1%.

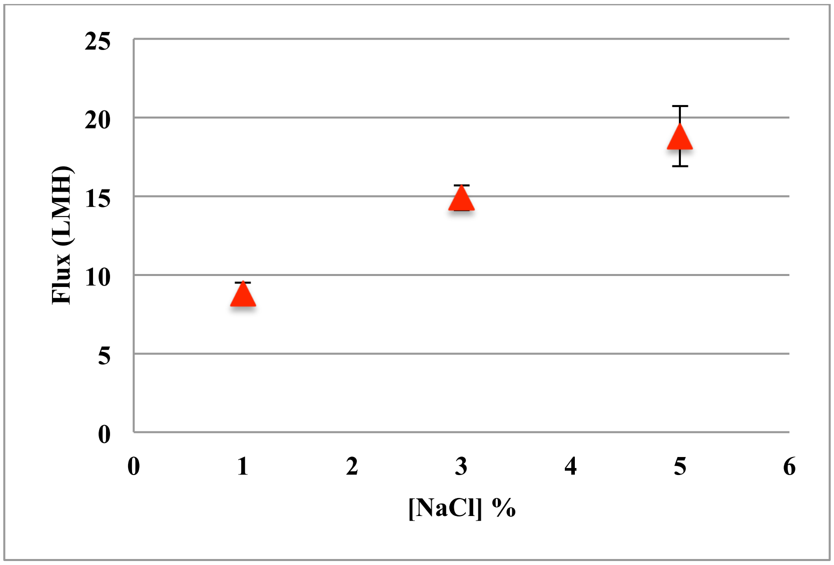

Figure 2: Water flux rate as function of NaCl draw solution concentration.

[NaCl] %	Na rejection	Cl rejection
1	99.942 ± 0.006	99.935 ± 0.003
3	99.967 ± 0.003	99.971 ± 0.003
5	99.968 ± 0.007	99.97 ± 0.01

Table 2: Summary of the results of ion rejection when NaCl is used as draw solution.

As stated before, NaCl draw solutions are widely used for FO applications. Figure 3 shows the graph of the water flux rate as function of $Ca(NO_3)_2$ draw solution concentration. The water flux rate increased with concentration for 5 and 10% w/w $Ca(NO_3)_2$ draw solution. However, at 15% w/w, there was not an increase in the water flux rate as expected. The reason for this can be hypothetically attributed to external concentration polarization.[6] Because 15% w/w is a very high concentration, it will cause accumulation of the $Ca(NO_3)_2$ in the support of the membrane, which results in the reduction of water flux. Table 3 summarizes the ion rejection when $Ca(NO_3)_2$ is used as draw solution at 5, 10 and 15% w/w. Porifera membrane showed that independent of the concentration of the draw solution, it rejects over 99.9% of the ions and its salt back-flux from draw solution to feed is ≤ 0.1%. The urea concentration of the feed did not show any significant impact in the ion rejection capacity of the membrane. Even when the highest urea concentration is 5 times higher, there are no statically valid differences as a function of urea concentration.

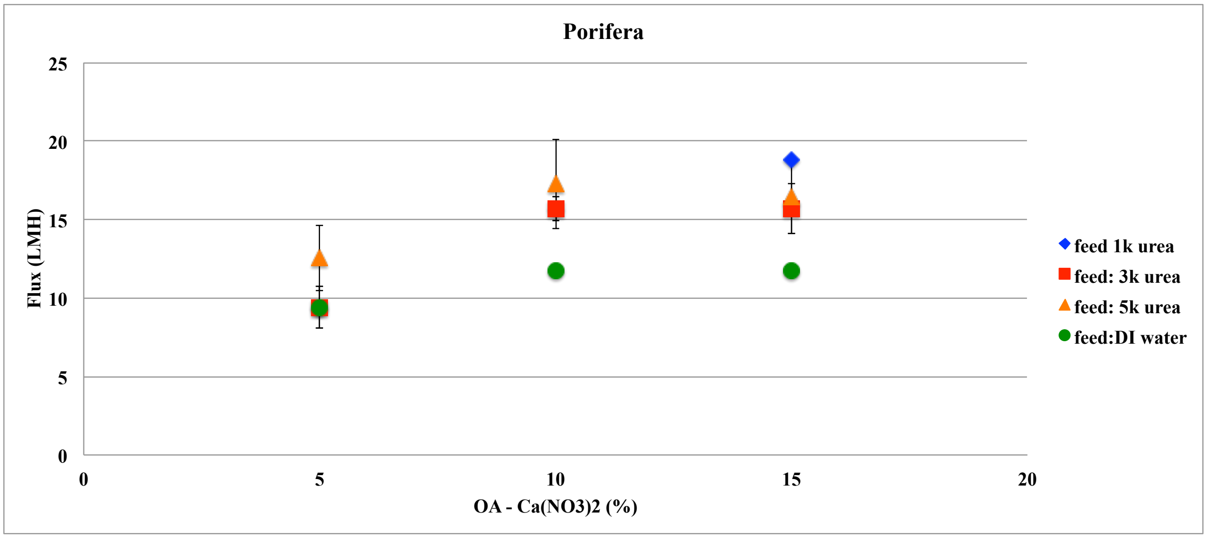

Figure 3: Graph of the water flux rate as function of $Ca(NO_3)_2$ draw solution concentration.

[urea] ppm	$[Ca(NO_3)_2]$ %	Ca^{+2} Rejection %	$(NO_3)^-$ Rejection %
1000	**5**	99.980 ± 0.003	99.983 ± 0.007
	10	99.989 ± 0.007	99.991 ± 0.007
	15	99.994 ± 0.001	99.995 ± 0.001
3000	**5**	99.988 ± 0.002	99.990 ± 0.002
	10	99.993 ± 0.005	99.993 ± 0.004
	15	99.94 ± 0.09	99.9 ± 0.1
5000	**5**	99.98 ± 0.02	99.98 ± 0.1
	10	99.991 ± 0.002	99.993 ± 0.001
	15	99.991 ± 0.003	99.993 ± 0.003

Table 3: Summary of the results of ion rejection when $Ca(NO_3)_2$ is used as draw solution.

In order to evaluate the urea rejection, urea in DI water (1000, 3000 or 5000 ppm) was used as feed and each urea concentration was tested with $Ca(NO_3)_2$ draw solution at 5, 10 and 15% w/w. To calculate the urea rejection, the following equation was used:

$$\%\ \text{urea rejection} = \frac{C_{Fi} - C_{DSf}}{C_{Fi}}(100) \qquad (2)$$

Where C_{Fi} is the initial TOC concentration (ppm) of the feed solution and C_{DSf}= final TOC concentration (ppm) of the draw solution. Table 4 summarizes the results of the TOC analysis. Since the feed was only urea and DI, the TOC values are directly related to urea, the only source of organic carbon. An average of 94.4 ± 0.9 % urea rejection was observed over the 60-minute experiments. In order to test the Porifera membrane for a real application, three test using raw human urine as feed. 10% w/w $Ca(NO_3)_2$ was used as draw solution since it was the concentration to show highest water flux rate across the membrane without concentration polarization effect.

Each test was performed for 90 minutes. Table 5 summarizes the Ion Analysis tests and Table 6 the TOC results. From Table 5, it can be observed that the human urine -feed contains many anions and cations and that the membrane shows a high ion rejection capacity and none of them was detected in the final draw solution. More important, ammonium $(NH_4)^+$, product of the urea decomposition, was completely rejected. Ca^{2+} and $(NO_3)^-$

rejections are 99.03% and 99.88%, respectively. Salt back-flux from draw solution to Feed is < 0.97%. From Table 6, it can be observed that TOC values of urine are higher than the concentrations previously tested (1000 – 5000 ppm) because human urine contains many other compounds, different from urea, like vitamins and hormones that contain organic carbon. However, the membrane showed to have an average TOC rejection, 99.2 ± 0.1 %.

[urea] (ppm)	$[Ca(NO_3)_2]$ (%)	TOC Feed initial (ppm)	TOC Feed final (ppm)	TOC DS initial (ppm)	TOC DS final (ppm)	TOC rejection (%)
1000	**5**	182 ± 28	200 ± 28	< 0.5	12 ± 6	93 ± 2
	10	176 ± 8	174 ± 4	< 0.5	9.9 ± 0.1	94.4 ± 0.2
	15	184 ± 6	193 ± 8	< 0.5	11.4 ± 0.9	93.8 ± 0.6
3000	**5**	497 ± 18	482 ± 17	< 0.5	24 ± 5	95 ± 1
	10	508 ± 15	522 ± 21	< 0.5	32 ± 7	94 ± 1
	15	529 ± 29	534 ± 60	< 0.5	33 ± 5	93.8 ± 0.8
5000	**5**	971 ± 62	936 ± 47	< 0.5	43 ± 8	96 ± 1
	10	905 ± 41	905 ± 37	< 0.5	45 ± 9	95 ± 2
	15	958 ± 72	937 ± 64	< 0.5	54 ± 19	95 ± 2

Table 4: Summary of the TOC results - urea rejection

	Sample	Na	NH4	K	Mg	Ca	Cl	NO3	PO4	SO4
Run 1	**Feed initial**	2835	576	892	124	264	3577	45.3	3069	2140
	Feed final	2807	598	873	131	276	3587	51.4	2896	2185
	DS initial	ldl	ldl	ldl	ldl	16953	ldl	53638	ldl	ldl
	DS final	ldl	ldl	ldl	ldl	17784	ldl	53019	ldl	ldl
Run 2	**Feed initial**	3180	495	846	133	283	3762	50.7	2625	1578
	Feed final	3053	462	794	121	259	3383	67.2	2624	1436
	DS initial	ldl	ldl	ldl	ldl	17455	ldl	53814	ldl	ldl
	DS final	ldl	ldl	ldl	ldl	17700	ldl	54801	ldl	ldl
Run 3	**Feed initial**	4162	456	1051	121	242	5353	209	1774	1550
	Feed final	4882	456	1064	120	239	5226	204	1573	1551
	DS initial	ldl	ldl	ldl	ldl	17592	ldl	53211	ldl	ldl
	DS final	ldl	ldl	ldl	ldl	17995	ldl	54865	ldl	ldl

Table 5: Summary of Ion Analysis for raw urine test. Values are in ppm units.

***ldl = less than the detection limit at the dilution required**

Run	TOC Feed initial (ppm)	TOC draw sol. final (ppm)	TOC rejection %
1	8314	59.3	99.28674525
2	7097	60.1	99.15316331
3	6641	63.4	99.0453245

Table 6: TOC results for test using raw urine as feed and 10% $Ca(NO_3)_2$ as draw solution.

IV. Conclusion

Based on the obtained results, Porifera membranes have high ion rejection, and urea rejection. When using a NaCl draw solution, Porifera membranes showed higher water flux rates than commercially available FO membranes. Porifera membranes reject over 99.9% of all ions to which it was exposed and therefore the salt back-flux from draw solution to feed is ≤ 0.1%. The urea concentration of the feed did not affect the ion rejection capacity of the membrane. High urea rejection was also achieved; being the lowest value was 93 ± 2%. However, Porifera membrane showed to have better urea rejection at higher concentrations (5000 ppm). When raw human urine was used, the membrane rejected 94.4 ± 0.9% of the TOC present in the feed.

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