

FOULING RESISTANT REVERSE OSMOSIS MEMBRANES

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ABSTRACT

Selective membranes have been used to separate solutes from the solvents in which the solutes are dissolved or suspended. Examples of such membranes are reverse osmosis (RO) membranes, ultrafiltration (UF) membranes, and microfiltration (MF) membranes, listed in the order of increasing pore size. RO membranes pass water, but reject salts and also organic solutes with molecular weight greater than 100 and are in general used for water purification including desalination of brackish water and seawater. However, one of the main problems in the membrane applications is the fouling of the membranes by solutes in natural water or industry effluents or municipal waste waters. The fouling solutes deposit on the membrane during operation to reduce water permeability and also sometimes solute rejection. Thus it is desirable to make the membranes resistant to the deposit of the foulants. The foulants are attracted to the membrane surface by hydrophobic interaction and/or charge attraction between the solutes and the membrane surface in addition to colloidal deposits.

This paper particularly deals with new fouling resistant RO membranes which are made more hydrophilic and less charged or charged with the same charge as the foulants to reduce hydrophobic interaction and charge attraction or to increase charge repulsion, respectively. The fouling resistant membranes were recently manufactured by Saehan Industries, Inc in Korea via coating RO membranes with hydrophilic monomers followed by polymerization and cross-linking reaction. The fouling resistant RO membranes showed much less flux reduction than the regular RO membrane when both membranes were subjected to 30 ppm dry milk, 50 ppm a cationic surfactant, 50 ppm a nonionic surfactant and 50 ppm humic acid, respectively.

The coated membranes were characterized in terms of membrane surface charge (zeta potential) and hydrophobicity (contact angle). The coated membranes showed much less negative charge than the regular uncoated membrane, but the contact angle of the coated membrane was about the same as the regular membrane. The membrane surface charge was controlled using various coating compounds. The membranes with various surface charges were dyed with a cationic dye such as methylene blue. The intensity of dyeing was linearly correlated with the degree of the negative charge on the membranes. The regular uncoated membrane was dyed the most since it has the most negative charge. The membrane fouling by the cationic surfactant was also linearly correlated with the degree of the negative charge on the membranes. The membrane fouling by the nonionic surfactant and humic acid had some relation with hydrophobic interaction between the foulants and the membranes. The membrane fouling by the dry milk appeared to be influenced by a mixture of hydrophobic effect, charge effect and some colloidal deposits.

In a field test using 8040 elements, the fouling resistant membrane maintained much higher permeability than the regular membrane when both are fed with an industry waste water at Hyundai Motor Co. for about 40 days. The fouling resistant RO membrane has been successfully in operation for treating waste water at Samsung Electronics Co. for about five months.

INTRODUCTION

RO membrane processes are becoming the preferred method for water purification since they are energy efficient and also highly efficient in removing dissolved solutes and contaminants from water. However, one main problem of the processes is the membrane fouling which is ascribed to the deposit of fouling solutes on the membrane. The membrane fouling manifests itself in a progressive decline of membrane flux over time under constant pressure operation. Water contaminants responsible for fouling membranes are represented as follows: suspended, colloidal, and dissolved matters. Suspended matters are larger particles and can efficiently be removed from the water using filtration or sedimentation. Thus, colloidal matters and dissolved solutes are primarily responsible for membrane fouling when they are deposited on the membrane surface during operation. The foulants are attracted to the membrane surface by hydrophobic interaction and/or charge attraction between the solutes and the membrane surface.

This paper particularly deals with new fouling resistant RO membranes which are made more hydrophilic and less charged or charged with the same charge as the foulants to reduce hydrophobic interaction and charge attraction or to increase charge repulsion, respectively. The fouling resistant membranes were recently manufactured by Saehan Industries, Inc in Korea via coating RO membranes with hydrophilic monomers followed by polymerization and cross-linking reaction. The coated membranes were characterized in terms of membrane surface charge (zeta potential), hydrophobicity (contact angle) and surface roughness by atomic force microscopy (AFM). The surface roughness of the membranes did not change much before and after the coating. Hence, the coated membranes are not expected to exert fouling resistance to the deposit of colloids any better than the uncoated membrane, since the roughness of the membrane surface most significantly influenced the rate and extent of fouling by colloidal deposit (1).

On the other hand, the surface charge and the hydrophobicity of membranes in general are reported to influence membrane fouling (2). The membrane surface charge was controlled using various coating monomers in such a way that the negative charge of the uncoated membrane (control) was decreasing gradually. Membrane samples with varying degree of hydrophobicity were also prepared. These membrane samples were exposed to a feed water containing a cationic dye, a cationic surfactant, dry milk, a nonionic surfactant and humic acid, respectively. The foulants were chosen to simulate a foulant in natural water (humic acid), industry and municipal waste water (surfactants), and food processing (dry milk).

EXPERIMENT

Membranes used in this study were high flux reverse osmosis (RO) membranes (BL grade from Saehan Industries, Inc., Korea) and were coated with proprietary hydrophilic monomers followed by cross-linking polymerization reaction. Dodecyltrimethylammonium bromide (Aldrich, Milwaukee) and methylene blue (Aldrich) were used as a cationic fouling agent. Triton X-100 (Aldrich), humic acid (Aldrich) and instant nonfat dry milk (Real) were used as a source of a nonionic surfactant, natural organic matter and proteins, respectively. Membranes were dyed with methylene blue by dipping the membranes in the dye solution (0.01%) for about 15 seconds followed by rinsing in DI water. Membrane surface charge (zeta potential)(3) was measured with electrokinetic analyzer (BI-EKA, Brookhaven Instruments Corp., Holtsville, New York). Membrane hydrophobicity was determined with contact angle measurement (AST Products, Billerica, Massachusetts).

A bench scale cross-flow unit equipped with 6 flat cells, employing 6 flat sheet membrane specimens, was used to measure initial water flux and salt rejection using 2000 ppm NaCl at a pressure of 225 psi. The membrane fouling experiment was carried out by adding 50 ppm dodecyltrimethylammonium bromide and 50 ppm Triton X-100 at pH 6.5, and 50 ppm humic acid and 30 ppm dry milk at pH 7, respectively to the feed water followed by circulating the feed water through the test unit for 4 hours, and then by measuring the reduced flux under the same conditions as above.

RESULTS and DISCUSSION

Table 1 shows the initial flux and salt rejection of five coated membranes (sample 1 to 5) and one uncoated membrane (sample 6) (control), and the flux and salt rejection of the membranes after being exposed to 50 ppm dodecyltrimethylammonium bromide (DTAB). The flux of the coated membranes decreased less in percentage than the control, indicating the hydrophilic coatings were helpful in reducing the adsorption of the cationic surfactant. The results in Table 2 from using 30 ppm dry milk as a foulant exhibits a similar trend that the coated membranes lose less flux in percentage than the control.

Table 1. Flux and Salt Rejection before and after Exposure to DTAB (Cationic Surfactant) at pH 6.5

Sample	Flux (gfd)	Rejection (%)	Flux (gfd)	Rejection (%)	Flux decline(%)
	=> DI washing / 2000ppm NaCl addition		=> 50ppm Cationic Surfactant addition		
1	32.5	98.2	21.2	99.2	34.9
2	31.8	98.6	20.4	99.3	36.0
3	28.4	98.2	17.4	99.1	38.5
4	28.5	98.9	17.7	99.3	38.0
5	32.7	98.3	19.1	99.3	41.6
6	57.4	98.4	25.1	99.1	56.2

Table 2. Flux and Salt Rejection before and after Exposure to Dry Milk at pH 7

Sample	Flux (gfd)	Rejection (%)	Flux (gfd)	Rejection (%)	Flux decline(%)
	=> DI washing / 2000ppm NaCl addition		=> 30ppm Dry Milk addition		
1	41.3	98.2	23.5	99.2	43.0
2	33.1	98.5	17.5	99.3	47.3
3	34.6	98.2	17.4	99.4	49.7
4	43.9	98.1	20.8	99.2	52.6
5	44.9	98.3	21.7	99.2	51.8
6	73.6	98.2	27.9	99.0	62.0

One may notice that the initial flux of the uncoated membrane (control) is much higher than that of the coated membranes and suspect that the initial high flux may cause the foulants to deposit more on the membrane because more foulants are brought to the membrane by the higher water permeation through the membrane. This may be true to a certain extent. The flat cell test unit is not equipped with a pressure control for each individual cell. Thus the water permeation rate of each membrane could not be controlled. However, when sample 1 and the control membranes were made into spiral wound elements (1812) and 30 ppm dry milk aqueous solution were circulated through the elements at 120-160 psi for 4 hours, starting with an equal initial permeation rate for both samples by adjusting the valve of the concentrate side, still the coated membrane (sample 1) lost less flux in percentage than the control as shown in Fig. 1.

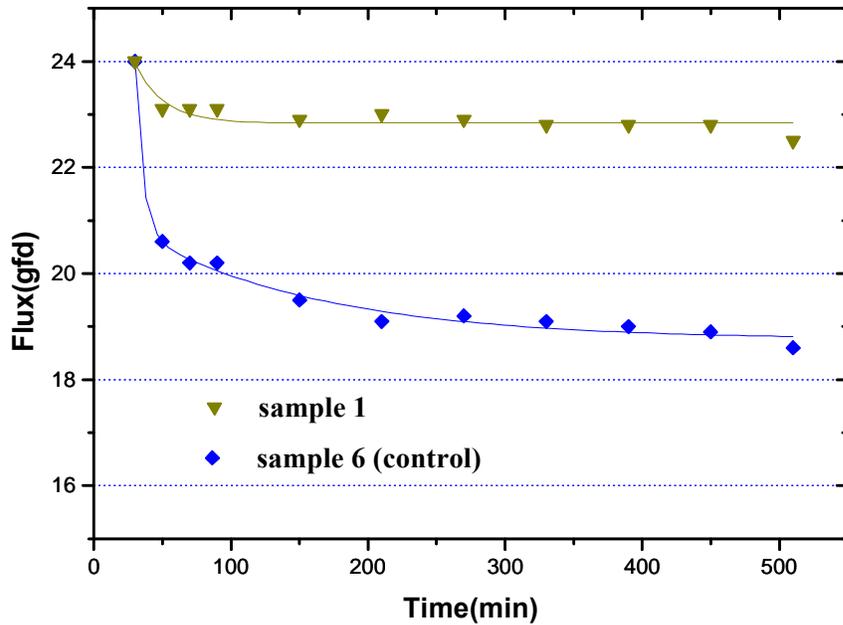


Fig.1. Flux Decline from Equal Initial Flux of Coated(1) and Uncoated(6) Membranes after subjected to 30 ppm dry milk.

Fig. 2 shows the same trend as Fig. 1 for the element tests starting with an equal initial flux using the cationic surfactant. The coated membrane (sample 1) still lost less flux in percentage than the control.

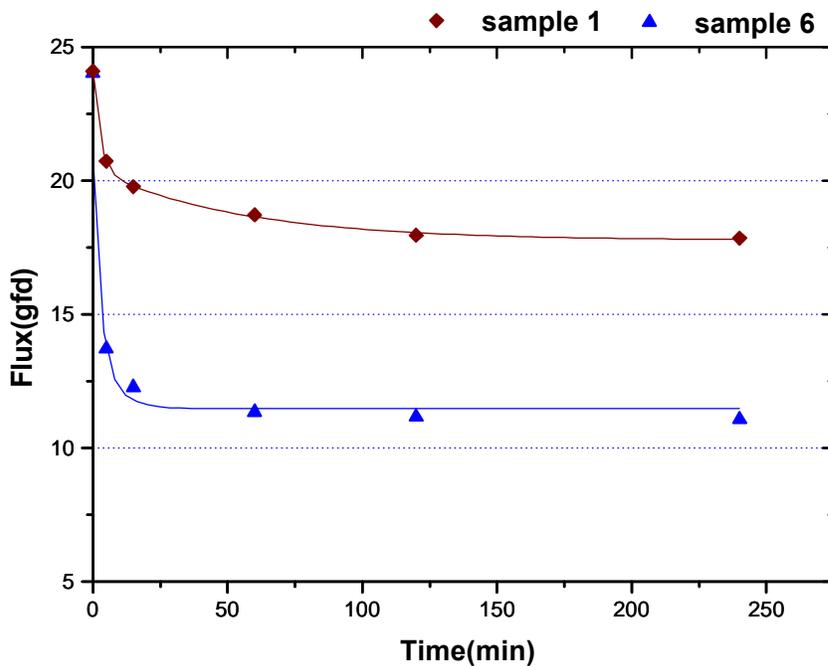


Fig. 2. Flux Decline from Equal Initial Flux of Coated(1) and Uncoated(6) Membranes after exposure to 50 ppm DTAB (a cationic surfactant)

Table 3 shows the flux decline of samples 1 to 5 and sample 6 (control) after being exposed to 50 ppm Triton X-100 (nonionic surfactant). The flux of the coated membranes decreased less in percentage than the control, indicating the hydrophilic coatings deter the adsorption of the nonionic surfactant. Fig. 3

shows the same trend as Fig. 1 for the element tests starting with an equal initial flux using the nonionic surfactant. The coated membrane (sample 1) still suffered less flux loss in percentage than the control.

Table 3. Flux and Salt Rejection before and after Exposure to Nonionic Surfactant at pH 6.5

Sample	Flux (gfd)	Rejection (%)	Flux (gfd)	Rejection (%)	Flux decline(%)
	=> DI washing / 2000ppm NaCl addition		=> 50ppm Nonionic Surfactant addition		
1	27.9	98.6	23.9	99.1	14.3
2	25.6	98.6	20.6	99.3	19.7
3	21.8	98.2	17.8	99.0	18.4
4	19.0	98.4	15.0	99.4	20.9
5	22.9	98.3	18.5	99.3	19.4
6	55.6	98.1	34.6	99.1	37.8

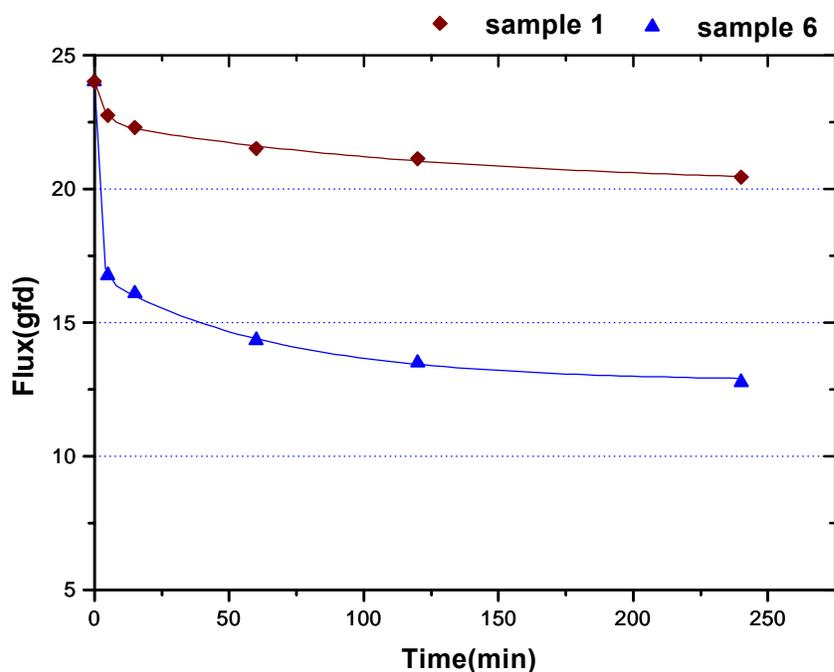


Fig. 3. Flux Decline from Equal Initial Flux of Coated(1) and Uncoated(6) Membranes after exposure to 50 ppm Triton x-100 (a nonionic surfactant)

Therefore, the above results suggest that different permeation drag may not be the deciding factor in fouling the membranes. Rather, other factors such as charge attraction and hydrophobic interaction appear to be more influencing.

Table 4 shows the flux decline of samples 1 to 5 and sample 6 (control) after being exposed to 50 ppm humic acid at pH 7.5. The flux of the coated membranes decreased less in percentage than the control, indicating the hydrophilic coatings reduce the adsorption of the humic acid.

Table 4. Flux and Salt Rejection before and after Exposure to Humic acid at pH 7.5

Sample	Flux (gfd)	Rejection (%)	Flux (gfd)	Rejection (%)	Flux decline(%)
	=> DI washing / 2000ppm NaCl addition		=> 50ppm Humic acid addition		
1	30.7	98.7	29.7	99.3	3.4
2	24.3	98.5	23.2	99.1	4.4
3	24.3	98.6	22.6	99.3	6.7
4	17.4	98.7	16.5	99.0	5.4
5	23.8	98.7	22.3	99.0	6.5
6	50.8	98.0	40.1	98.6	21.0

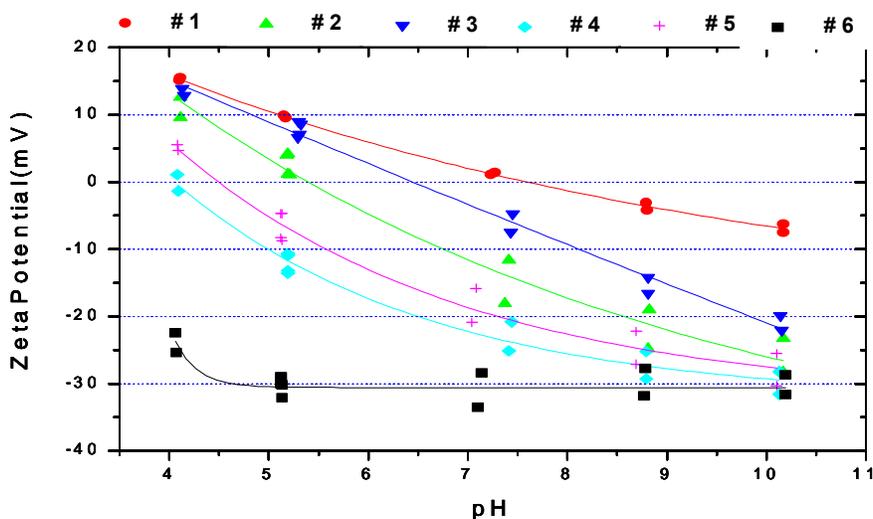


Fig.4. Zeta Potential of Coated(1-5) and Uncoated(6) Membranes.

Fig. 4 shows zeta potential (surface charge) of the six samples. The control (sample 6) exhibits the most negative potential. The zeta potential of the coated membranes decreases from sample 1 (the least negative) to more negative (sample 4 and 5). The zeta potential of the six membranes correlates fairly well with the extent of the fouling of the membranes (percent flux decline) by DTAB (cationic surfactant) as shown in Table 1. In other words, the more negatively charged the membrane, the greater the flux decline of the membrane due to the cationic surfactant fouling. This phenomenon is explainable in terms of the attraction of the oppositely charged ions. A similar trend is observed in the case of the membrane flux decline due to the dry milk as shown in Table 2. However, the fouling trend by the dry milk could not be explained well based on charge attraction, since most proteins are negatively charged at pH 7. The negatively charged proteins should be repelled well by negatively charged membranes such as sample 6 (control) to result in the least flux decline, but the experimental data shows the opposite way.

In order to study further the charge effect of the dry milk on the membrane fouling, the fouling experiment was conducted at various pH, assuming the proteins may have more negative charge at higher pH, and the results are shown in Table 5.

Table 5. Flux decline at various pH due to fouling by dry milk

Type of membrane	Flux decline (%) at pH3	Flux decline (%) at pH5	Flux decline (%) at pH7	Flux decline (%) at pH9	Flux decline (%) at pH10
Sample 1	11.1	16.6	18.1	14.1	2.8
Sample 6	32.6	38.4	39.1	48.4	12.0

As the results show, there is no reverse in fouling tendency between the two samples, indicating no isoelectric point in the range from pH 3 to 10. The uncoated membrane (sample 6) was always fouled much more than the coated membrane (sample 1) at the pH range. The only change in the results was that both samples were fouled much less at pH 10 than the other pHs, though the trend remained the same. This suggests a possibility that at pH 10 the dry milk may be more soluble to result in fewer number of protein aggregates and thus cause less fouling to the membranes. Thus it appears that there is no charge effect on the membrane fouling by the dry milk.

Assuming that a hydrophobic interaction might play a strong role here, contact angles of the samples were measured as shown in Table 6. A puzzling thing is that there is not a good correlation between the contact angles and the flux decline (fouling). The control (sample 6) has the lowest contact angle (presumably the most hydrophilic), but yet shows the most fouling. This suggests that the contact angle may not be a good presentation of hydrophobicity. However, except sample 6 (control), samples 2 to 5 were more hydrophobic and thus experienced more flux decline than sample 1 as shown in Table 2. Hydrophobic effect on the fouling may work here to a certain extent. Surface roughness may not offer an explanation for the fouling trend, since there is not much difference in surface roughness between samples 1 and 6.

Judging from the fouling data at pH 10 as mentioned above, aggregates of proteins could exist in the dry milk solution and, if carboxyl groups having negative charges are trapped inside the aggregates, then the protein aggregates might have some positive charges. The aggregates with some positive charges could foul sample 6 more than sample 1. Streaming potentials of the dry milk solution should be measured to verify this hypothesis.

Table 6. Contact Angle of Coated(1-5) and Uncoated(6) Membranes

Sample	#1	#2	#3	#4	#5	#6
Contact angle	45.1	63.4	65.3	60.9	61.2	44.1

The fouling trend of samples 1 to 6 by Triton X-100 (nonionic surfactant) is roughly correlated with hydrophobicity of the samples (contact angles) except sample 6 as shown in Table 3. No explanation could be offered yet why sample 6 showing the lowest contact angle was fouled the most among the samples.

Humic acid is part of natural organic matter (NOM) present in natural water coming from decaying plants. NOM exerts serious membrane fouling problems in the purification of waters from natural sources (4). Humic acid fouled very lightly samples 1 to 5 and moderately sample 6 (uncoated). This humic acid from Aldrich might have low molecular weight humic acid in predominant portion, which could exert less fouling than higher molecular weight. However, the fouling trend shows a correlation with hydrophobicity of sample 1 to 5 except sample 6 as shown in table 4. If there was repulsion between negatively charged humic acid and negatively charged membrane surface, samples 4 and 5

would be the least fouled among samples 1 to 5 as mentioned in the literature (5). But the data shows the opposite way. Thus hydrophobic interaction between the humic acid and the membranes may be more influential on fouling than the charge repulsion in the case of this humic acid.

A good correlation between the adsorption of methylene blue (a cationic dye) and the zeta potential has been observed. The intensity of the adsorbed dye appears to increase linearly with an increase in the negative charge of the membrane (picture is not shown here). The degree of membrane fouling by DTAB (a cationic surfactant) is also proportional to the negative charge on the membrane surface as shown in Table 1. The results support the view that membrane fouling due to charge attraction can be characterized better than hydrophobic interaction or colloidal deposit.

Fouling resistant membranes similar to sample 1 was manufactured commercially and have been on long term field test. Fig. 5 shows the flux decline of 8040 elements from the fouling resistant membrane and the regular membrane over 40 days when they were exposed to the waste water at Hyundai Motor Co. As the result shows, the flux decline of the regular membrane was steeper than the fouling resistant membrane, which maintained much higher flux than the regular membrane after 40 days.

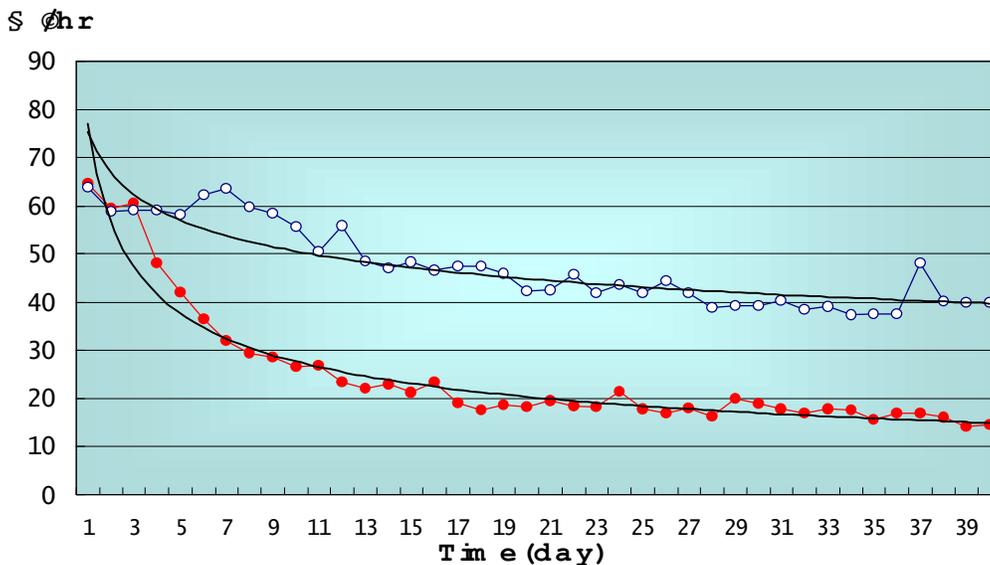


Fig. 5. Comparison study on the flux decline of 8040 elements of the fouling resistant and the regular membranes over 40 days at Hyundai Motor Co.

Fig. 6 shows daily plot against permeate water flow and differential pressure of the waste water treatment system using 8040 elements made from the fouling resistant membrane at Samsung Electronics Co., over 5 months. The result shows the permeate water flow remained fairly steady and the differential pressure was maintained within the system design, requiring less cleaning periods.

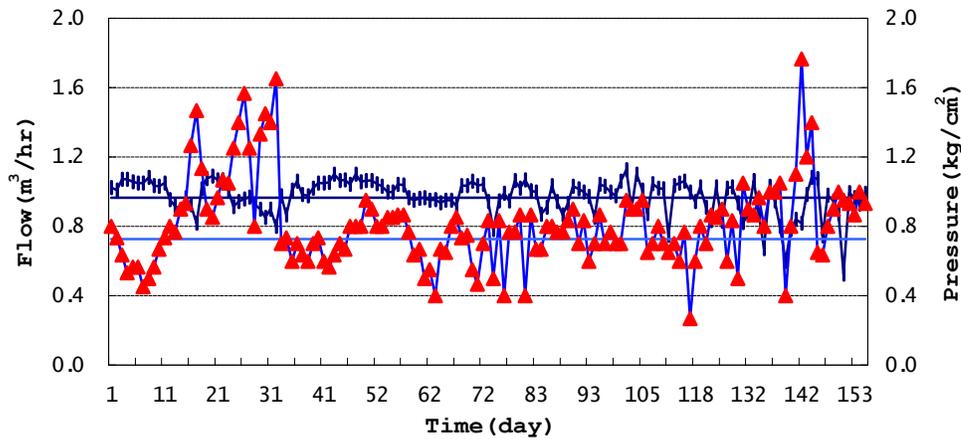


Fig. 6. Permeate water flow of the commercial system using the fouling resistant membrane and system differential pressure over 5 months at Samsung Electronics Co.

CONCLUSION

High flux reverse osmosis membranes manufactured by Saehan Industries, Inc. in Korea were coated with hydrophilic monomers followed by cross-linking polymerization reaction. The coated membranes showed a fouling resistance to a feed water containing 50 ppm dodecyltrimethylammonium bromide (DTAB) (a cationic surfactant), 30 ppm dry milk, 50 ppm Triton X-100 (a nonionic surfactant) and 50 ppm humic acid, respectively, compared with the uncoated membrane (control). The extent of the membrane fouling (flux decline) by the cationic surfactant at pH 6.5 appears to have a linear correlation with the zeta potential (membrane surface charge). The extent of methylene blue (a cationic dye) adsorption on the membranes is also proportional to the membrane surface charge. The two results show that the charge attraction between the oppositely charged foulants and the membrane is an easily characterizable mechanism of the membrane fouling.

The membrane flux decline by the nonionic surfactant at pH 6.5 was supposed to be due to hydrophobic interaction between the membrane and the surfactant. The experimental result shows that membranes having higher contact angle lost more flux by the surfactant. The control membrane without the hydrophilic coating actually exhibited the lowest contact angle, but suffered the most flux loss by the surfactant. This could not be explained well. The membrane fouling by humic acid at pH 7.5 which fouled the membranes much less than other foulants appeared to be more influenced by hydrophobic interaction rather than charge repulsion between the negatively charged humic acid and the membranes, since the most negatively charged control membrane was fouled the most.

The membrane fouling by dry milk was quite severe compared with other foulants. The fouling mechanism could be complex. Hydrophobicity and colloidal fouling may be responsible partially for the fouling. If the dry milk was charged positively, the fouling could have some linear relationship with the negative charge on the membranes.

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