Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.940640

57 (2016) 323–334
January

Taylor & Francis
Taylor & Francis Group

Nanofiltration membrane cleaning characterization

Ahmed Al-Amoudi

Saline Water Desalination Research Institute (SWDRI), Saline Water Conversion Corporation (SWCC), P.O. Box 8328, Al-Jubail 31951, Saudi Arabia, email: rdc@swcc.gov.sa; aalamoudi2@swcc.gov.sa

Received 19 February 2014; Accepted 16 June 2014

ABSTRACT

In membrane process industries, membrane cleaning is one of the most important concerns from both economical and scientific points of view. Though cleaning is important to recover membrane performance, an inappropriate selection of cleaning agent may result into unsatisfactory cleaning or irreparable membrane. In this study, the cleaning performance has been studied with measurements of membrane contact angle values, surface roughness, zeta potential and pore size by positron annihilation spectroscopy, and salt rejection as well as flux measurement. Thin-film nanofiltration membranes such as DK, provided by GE-Osmonics are used in this study. Tests were carried out with virgin DK. Several cleaning agents were investigated, some of them were of analytical grade such as HCl, NaOH, and others such as SDS mix agents were commercial grade agents that are already in use in commercial plants. Contact angle values, surface roughness, zeta potential and pore size, and salt rejection as well as flux of virgin membranes before and after chemical cleaning were measured and compared. The membrane contact angle values, surface roughness, zeta potential, and pore size measurements with and without chemical cleaning of virgin membranes were measured and revealed very interesting results which may be used to characterize the membrane surface cleanliness. The membrane contact angle values, surface roughness, zeta potential, and pore size results revealed that the cleaning agents are found to modify membrane surface properties. The details of these results were investigated and are reported in the paper. The salt rejection levels of divalent ions before and after cleaning by high- and low-pH cleaning agents were looked into it.

Keywords: Nanofiltration; Membrane; Cleaning; Cleaning agents

1. Introduction

The separation characteristics of nanofiltration (NF) membrane stand between ultrafiltration (UF) and reverse osmosis (RO). Membrane selectivity has often been attributed to the mechanism of the molecular-sieving properties of UF and the diffusion properties of RO. It is generally recognized that membrane hydrophobicity/hydrophilicity, pore size (and their distribution), and surface charge may be important factors determining separation performance and the fouling tendency of NF membranes [1–3]. The interaction of organic and inorganic colloidal substances with membrane surfaces in aqueous media is also an important factor, which depends not only on the

Presented at the Conference on Desalination for the Environment: Clean Water and Energy
11–15 May 2014, Limassol, Cyprus

membrane surface charge and hydrophobicity/hydrophilicity of the surface but also on the membrane pore size and pore size distribution.

A large number of chemical cleaning agents are commercially available. Five categories of cleaning agent commonly used are: alkalis, acids, metal chelating agents, surfactants, and enzymes [4,5]. Commercial cleaning products usually have a mixture of these chemicals but their actual composition is often unknown. The choice of the optimal cleaning agent or chemical composition depends on feed characteristics. For example, acid cleaning is suitable for the removal of precipitated salts, such as $CaCO_3$, while alkaline cleaning is used to remove adsorbed organics [6].

Flux measurement directly reflects the cleaning process. It is generally accepted that flux decline in aqueous solutions (containing organic and inorganic molecules) is mainly caused by adsorption or crystallization, possibly enhanced by pore blocking and/or cake formation [7–9]. Effective chemical cleaning would, therefore, be necessary to detach different classes of foulants from the membrane and thereby restore its permeate flux characteristics [10]. Furthermore, the selection of appropriate chemical cleaning agents might be critical. This is because incompatible combinations of cleaning agent and membrane material could lead to irreversible flux loss and unnecessary costs due to excessive chemical use resulting in reduction of membrane life [4,10]. The complexity of cleaning processes has not yet been addressed by many researchers and a detailed understanding is needed for a clear knowledge of these processes. Although cleaning is intended to restore the flux, it often deteriorates product quality and increases the cleaning frequency affecting plant availability.

It is my contention that the data produced by my investigations into assessing precisely the chemical cleaning processes by novel techniques, in order to reach the optimum cleaning processes to restore the flux without deteriorating the quality and thus, reduce the membrane replacement and energy lost during the operation can be considered to be a development of a scientific solution to solve specific problem. The information drawn from this work will allow significant improvements in the efficiency of potable water production which in turn will not only increase the viability and sustainability of the process but also will reduce significantly the total water cost and ultimately improve access for the end user. More to the point, the cleaning process can be improved and optimized using the novel techniques described here in order to eliminate the deterioration of the membrane active layer by the cleaning process. This can be implemented to any membrane system whether it is MF, UF, NF, or RO membranes.

In order to predict membrane separation performance, it is necessary to know the mean pore size and the pore size distribution at the membrane surface. The pore size distribution, the diffusion parameter, and the experimental water flux through the membrane were all used to calculate the retention as a function of the molecular weight and pressure for several different membranes. This makes it possible to determine retention curves at different pressures, and to calculate the variation of the MWC with pressure [10]. Bowen et al. [11,12], developed a method called the Donnan steric partitioning pore model (DSPM), which is based on the extended Nernst–Planck equation (modified to include steric effects) and a modified Donnan equation accounting for the sieving effect as well. A theoretical background description of the DSPM has been given in detail elsewhere [11,12]. The DSPM has been successfully used to describe retention of neutral solutes and ions on NF and UF membranes and on titanium membranes with NF membrane properties [13,14]. In previous work, an updated version of the DSPM was used [15,16]. Using this model offers the advantage of removing membrane thickness from the rejection equation because the NF-driving force is redefined in terms of an effective pressure as opposed to the volumetric flux. As a direct result, the rejection equation for uncharged solute becomes solely dependent on the pore radius. Therefore, experimental rejection setup at various levels applied effective pressures for a solute of known size will directly characterize the membrane pore radius. Al-amoudi et al. [17] reported that the updated DSPM method failed to provide any valuable information about the pore size of the untreated and treated NF virgin and fouled membranes.

It is well-established fact that chemical cleaning agents such as SDS, mixed agents, NaOH, and HCl are widely used in the applied industrial plants. The main objective of this work and previous works is to open-up the discussion of cleaning strategies with those who have applied such cleaning agents in their plants in order to restore the production and to ascertain whether a correlation exists between the flux and/or salt rejection and the data obtained from these techniques. Cleaning processes do regenerate the water produced, but simultaneously degrade its quality. Therefore, the efficiency of cleaning agents widely used in the industrial plants must be investigated thoroughly in the laboratory before they are used in industrial plants.

2. Experimental

2.1. Materials

2.1.1. Membrane

One specific type of commercial NF membrane, GE Osmonics DK flat sheet membrane was used in this study. DK thin-film membranes (TFM) are negatively charged having a proprietary active nanopolymer layer based on polypyperazinamide. The active top layer of DK consists of three sublayers; [these TFM were supplied by GE Osmonics, Florida, USA]. However, the molecular cut-off point for a DK NF membrane is 150–300 Dalton [18]. Prior to the experiments, all virgin NF membranes were soaked overnight with or without cleaning agents in high-purity water obtained from a Millipore ELix 3 unit.

2.1.2. Chemicals

The analytical grade salt used in these experiments was divalent magnesium sulfate-7-hydrite (Sigma–Aldrich). The salt concentration ions of the feed and product were measured via conductivity. High-purity water obtained from a Millipore Elix 3 unit (with a conductivity of less than 1 $\mu S\,cm^{-1}$) was used in these experiments at a pH of 5.8.

2.1.3. Cleaning agents

Two analytical grade chemicals (HCl and NaOH) and two commercial grade chemicals SDS (0.1%) and a mixture of trisodium phosphate (0.1%), sodium tripolyphosphate (0.1%), and EDTA (0.1%)) (TSP + EDTA + STP) were used as cleaning agents in the experiments. The commercial cleaning agents are similar to that used in the Umm-Lujj commercial NF plant [19].

2.2. Methods

2.2.1. Cleaning procedure

New membranes were used for each set of experiments. In one set of experiments, the virgin membranes were rinsed several times in demineralized water in order to remove any impurities from the virgin membranes. Bench scale experiments were carried out in this study. Several sets of experiments were carried out with different cleaning agents by soaking virgin membranes in cleaning agents overnight for 18 h and then starrier for 90 min. The treated virgin membranes were then soaked in high-purity water for a few hours and thoroughly rinsed using high-purity water in order to remove any remaining cleaning agents from the membrane surfaces.

2.2.2. Positron annihilation

Positron annihilation γ-ray spectra for the membranes were collected at different $E_{\rm in}$ with a Na-source-based magnetically guided positron beam system. The line-shape S parameter was determined as the ratio of the counts appearing in the central region (510.3–511.7 keV) to the total counts of the 511 keV and annihilation photo peak (506.8–515.2 keV) in the spectrum recorded with a Ge detector. The 3 annihilation of o-Ps could lead to γ rays with energies lower than 511 keV. The positron 3γ annihilation was characterized as the R parameter, which was determined as the ratio of the counts in a low-energy window (365.0–495.0 keV) to those in the 511 keV and annihilation photo peak (506.8–515.2 keV) in the spectrum obtained as a function of $E_{\rm in}$.

An intense pulsed-positron beam generated with an electron linear accelerator was used to measure the lifetimes of positrons at different $E_{\rm in}$. Lifetime data were recorded by determining the time interval between the timing signal from the pulsing system and the detection of an annihilation γ-ray using a BaF_2 scintillation detector. The recorded positron lifetime data were analyzed assuming three or four exponential components plus background to deduce the average lifetime τ_3 and relative intensity I_3 of the long-lived component of o-Ps. The free volume hole size was evaluated from τ_3 using Eqs. (1) and (2).

2.2.3. Streaming potential measurement

The zeta potential is an important and reliable indicator of the surface charge of membranes and it is now well recognized that charge or electrical potential properties of membranes have a very substantial influence on their filtration performance before and after cleaning.

Zeta potentials were determined with the electrokinetic analyzer (Anton Paar KG, Graz, Austria) based on the streaming potential method. Zeta potential as a function of pH was studied.

2.2.4. Contact angle measurements

The hydrophobicity/hydrophilicity of several samples of both treated and untreated virgin membrane was determined via contact angle measurement using the Fibro DAT 1100. The instrument consists of a syringe containing the test liquid, tubing through which the liquid is passed, a cannula through which the drop is delivered to the test chamber, a testing block onto which the substrate is mounted, and a CCD camera to record the change in dot profile.

2.2.5. Atomic force microscopy

Atomic force microscopy (AFM) is a high-resolution imaging technique that can be utilized to study the surface morphology of separation membranes. It is utilized to obtain three-dimensional topographical images of membrane surfaces up to atomic level resolution in air or in liquid by scanning a sharp tip, situated at the end of a microscopic cantiliever, over the surface. An additional advantage of this technique, other than the high resolution achieved, is that no special sample preparation is needed. No heavy-metal coating is required as in SEM and TEM techniques that might give some imaging artifacts and have a tendency to damage the membranes. A more true surface morphology of a polymeric membrane can be observed by AFM. The AFM may be used in a number of different modes: contact mode, non-contact mode, and tapping mode.

A piece of treated and untreated virgin of dimension 1 cm × 1 cm was placed onto metal sheet with stick glow in order to affix the membrane sample prior to any AFM measurement. The AFM used for imaging was a Dimension 3100 (Nanoscope 3, Vecco instruments, USA). Treated and untreated virgin NF TFM membrane surfaces were imaged in contact mode in salt solution (NaCl 0.1 M) using a tip with coated, unsharpened microlevers (MLCT-AUNM, Veeco, Cambridge, UK). The surface morphology was measured in liquid with scan rate of 1 Hz at 516 × 516 resolution in contact mode.

The membrane surface was also imaged in air (20°C, RH 40 ± 5.0%), via tapping mode. Tapping mode probes (Olympus, Japan) with a spring constant of 42 N/m and a nominal tip radius of 5 nm were used throughout. Images were obtained from areas of 5 × 5 μm and 1 × 1 μm at a scan rate of 1 Hz. All images were obtained with the same imaging parameters; amplitude set point, loading force, and scan rate. Topographical (height) and phase images were captured simultaneously, with five images captured from different locations on a surface.

2.2.6. Flux and rejection measurements

In order to characterize the cleaning efficiency, the flux and the rejection of divalent ($MgSO_4 \cdot 7H_2O$ at 2,482 ppm) salt were measured. Permeation and rejection experiments with divalent salt solutions in demineralized water were carried out using a laboratory-scale cross-flow recirculation test unit. The test unit consisted of a rectangular membrane cell, a feed reservoir, a variable speed gear pump, a flow meter to measure cross-flow, a balance for measuring filtrate flow, pressure transducers, a temperature control system, and a computerized data logging system. Detailed descriptions of the unit and instrumentation can be found elsewhere [18,20]. The pressure of the inlet and outlet was maintained at 400 kN m^2 and cross-flow rate was maintained at 0.35 l/min by employing variable speed drive. All experiments were carried out at a temperature of 25°C.

2.2.7. Model flux and rejection measurement protocol

A new piece of membrane was placed in the cell and water was then passed through the cell to wash out any impurities that might have been present. This procedure was repeated twice. Then, a $MgSO_4 \cdot 7H_2O$ model solution at 2,464 ppm concentration was passed through the membrane. The rejection was measured after 20 ml of permeate passed through the membrane. Then, the cell was washed thoroughly by circulating fresh water at the same pressure. This procedure was repeated once or twice with the new virgin membranes.

3. Results and discussion

Both untreated and treated virgin DK TFM with high- and low-pH cleaning agents were characterized using pore size measurement via the positron annihilation, AFM, zeta potential, and contact angle measurements as well as flux and salt rejection measurements. A correlation was found between the pore size, zeta potential, and contact angle measurements and AFM measurement for untreated and treated NF membranes, flux, and salt rejection.

3.1. Pore size (positron annihilation)

Based on earlier and present work, the effects of membrane pore size and surface state were determined. However, the effect of cleaning agents had pronounced effects on the pore size and surface state as well [18,21,22]. At high-pH values cleaning agents, consisting of SDS or a mixture of trisodium phosphate, sodium tripolyphosphate, and EDTA (recommended by the membrane manufacturer) had a marked effect on the pore size and the pore size expanded to 0.30 and 0.31 nm, respectively, when compared with pore size of untreated NF virgin membrane (0.277 nm) (Table 1) [1]. Whereas, at low-pH chemical cleaning with HCl had minor effect on the pore size of 0.28 compared with untreated NF virgin membrane of 0.277 nm. On the other hand, chemical cleaning agent of NaOH had expanded the pore size

Table 1
Results on the positron annihilation lifetime measurements

Sample	Note	Lifetime (ns)	Radius (nm)
1	Virgin membrane	1.90	0.277
2	Virgin membrane treated with SHMP+ EDTA	2.20	0.31
3	Virgin membrane treated with SDS	2.19	0.30
4	Virgin membrane treated with HCl	1.96	0.28
5	Virgin membrane treated with NaOH	2.0	0.29

from 0.277 to 0.29 nm. Thereby, the positron annihilation technique is a powerfull technique to measure the change in the pore size that had been affected by chemical cleaning agents.

3.2. Zeta potential measurement

The effects of temperature, pH, and the cleaning agents on membrane zeta potential were determined. The temperature was found not to have any significant effect on membrane zeta potential; however, the effect of pH and cleaning agents had pronounced effects on the surface charge and zeta potential. At high-pH values cleaning agents, consisting of SDS or a mixture of trisodium phosphate, sodium tripolyphosphate, and EDTA had a marked effect on the zeta potential of DK membranes when compared with other cleaning agents [1]. The results of the zeta potential vs. pH for the untreated NF TFM at 25˚C are considered. The virgin NF TFM of DK was positively charged at low pH with an isoelectric point between pH 3.9 and negatively charged at high pH [1].

3.3. Contact angle measurement

The contact angle measurement provides valuable information about the membrane surface state, and is also a reliable technique to assess the surface state of cleaned NF membranes. The contact angle results revealed that the cleaning agents modified the membrane surface properties of the virgin membranes. This study shows that the cleaning has a major effect on the performance of NF membranes and their surface properties. The contact angle measurements indicate that mixed and SDS cleaning agents had a very adverse effect upon the virgin NF membranes. The membrane surface properties were modified to the extent that the flux was increased by over 100% and the membrane hydrophilicity increased significantly (low contact angle measurement), indicating irreversible chemical reaction and adsorption on the membrane surface (Table 2). However, the NaOH and mix cleaning results revealed better performance showing a considerable cleaning efficiency, whereas use of HCl as a cleaning agent resulted in poor cleaning efficiency [21].

Table 2
Contact angle measurements for virgin NF DK, DL, and HL membranes cleaned with various cleaning agents [21]

Contact angle measurement	θ DK
Virgin NF	45.10
Cleaned virgin-HCl	45.66
Cleaned virgin-NaOH	39.45
Cleaned virgin-SDS	28.00
Cleaned virgin-mix	34.85

Note: The standard deviation of the results was less than 5%. The mix agent consisted of a mixture of trisodium phosphate (0.1%), sodium tripolyphosphate (0.1%), and EDTA (0.1%).

3.4. AFM analysis

The results of surface roughness obtained by AFM measurements reveal that the cleaning efficiency can be evaluated by this technique. For the cleaned membranes, the lowest surface roughness, with Ra = 2.1 (±18.4%) nm, was obtained for the virgin membrane cleaned with HCl (low pH cleaning) whereas the roughest surface area, with a Ra = 14.0 (±53.5%) nm, was obtained for the fouled membrane cleaned with mix agents (high pH cleaning) (Table 3). These results indicate that adsorption phenomena could be recognized by AFM techniques. Roughness is an important indication as to how a surface will interact with cleaning agent materials.

3.5. Flux and rejection

In order to obtain the experimental data to characterize the treated and untreated membranes, cross-flow unit was used to conduct the water filtration tests. Permeation experiments with divalent salt solutions were conducted utilizing a cross-flow

Table 3
Surface roughness of the DK NF membrane when cleaned with various cleaning agents

	Uncleaned		Cleaned with HCl		Cleaned with Mix		Cleaned with NaOH		Cleaned with SDS	
	Z	Ra	Z	Ra	Z	Ra	Z	Ra	Z	Ra
Virgin membrane (1 μm)										
Mean	18.5 ± 1.1	2.0 ± 0.3	58.8 ± 2.1	2.1 ± 0.3	50.7 ± 1.9	5.7 ± 0.9	51.0 ± 2.2	5.8 ± 1.0	81.0 ± 2.7	9.1 ± 1.0
Fouled membrane contact mode (liquid) 1 μm										
Mean	165.5 ± 20.7	14.8 ± 3.6	39.0 ± 15.6	12.8 ± 3.6	141.1 ± 19.7	14.0 ± 3.1	146.9 ± 24.3	13.1 ± 4.5	142.5 ± 27.9	13.9 ± 3.9

Note: The Mix agent consisted of a mixture of trisodium phosphate (0.1%), sodium tripolyphosphate (0.1%), and EDTA (0.1%).

Table 4
Flux of hydrated magnesium sulfate of virgin NF membrane standard deviation is less than 5%

	kg/m^2h
Untreated membrane	Virgin DK 5.6
Treated membrane by	
HCl	9.2
NaOH	14.5
Mix	17.6
SDS	16.1

recirculation test unit. Treated DK membranes were found to exhibit higher fluxes than for untreated virgin membranes when the model solution was used as feed. For example, the flux increased by more than double for the virgin membrane after it was cleaned with the high-pH cleaning agents. Highest flux (17.6 kg/m^2h) was achieved by treating the membranes with mix cleaning agent and lowest (9.2 kg/m^2h) using HCl cleaning compared with untreated membrane flux that was 5.6 kg/m^2h (Table 4). While the flux for NF membrane treated with SDS and NaOH was about 16.0 and 14.5 kg/m^2h, respectively. In order to characterize the cleaning efficiency, the rejection of the divalent ($MgSO_4{\cdot}7H_2O$ at 2,482 ppm) salts was measured using cross-flow recirculation test unit. The divalent rejection of $MgSO_4{\cdot}7\ H_2O$ for virgin DK TFM was about 96.5% (Table 5).

Table 5
Rejection of magnesium sulfate of virgin NF

	Rejection (%) DK
Untreated	96.4
Treated by HCl	96.0
Treated by NaOH	94.0
Treated by SDS	88.0
Treated by mix	92.4

The rejection of divalent ions in the case of virgin NF TFM cleaned by HCl, NaOH, and mix of 96, 94, and 92.4%, respectively, exhibited slightly close to untreated virgin membrane (Table 5). Conversely, in the case of SDS cleaning agents for virgin NF TFM, the rejection of divalent was found to exhibit significantly lower rejections (88%) than the untreated membrane (96.4%).

3.6. Correlation

Due to the low number of data, the correlation only give a preliminary indication of the possible correlation that could exist—more work would be needed to make the correlation more consistent. From this point of view, as mentioned in the objective, this study is intended to evaluate the validity of these techniques, whether it is possible to obtain useful information about the pore size, zeta potential, contact angle, and AFM measurements of membrane after cleaning or not, and also to find out whether a

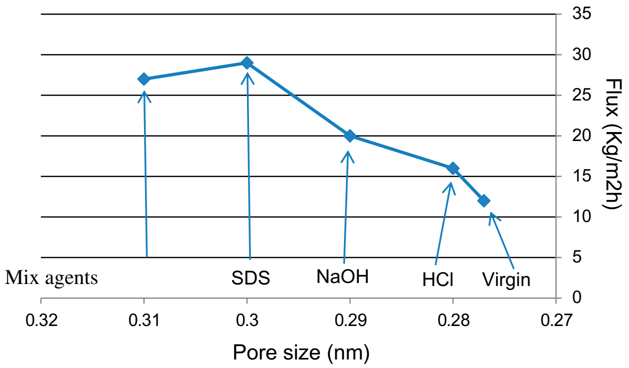

Fig. 1. The correlation between pore size and flux for virgin membrane cleaned by various cleaning agents.

correlation exist between the flux and/or salt rejection and the data obtained from these techniques. If it does, then subsequently the variation of cleaning concentration and the cleaning procedure will be worthy of study in order to find out what is the optimum cleaning system. The correlations figures between pore size and the flux as well as the salt rejection have shown very positive results. Correlations are found to exist for both untreated virgin NF membrane and treated virgin NF membrane. Nevertheless, the result obtained from the correlation between the pore size (free volume hole radii) and flux for the treated and untreated virgin membranes indicate that the radius of these membranes conveys very useful information.

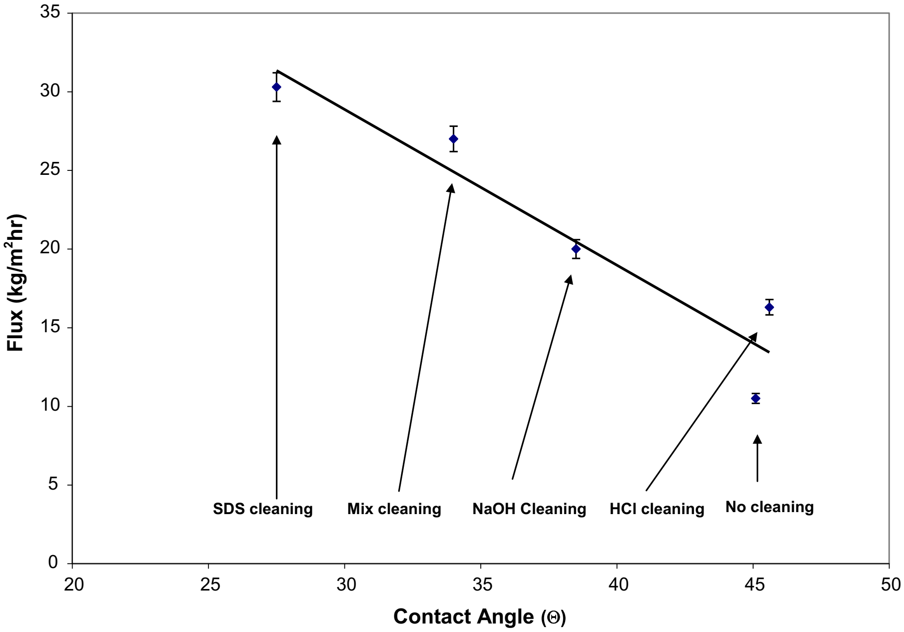

Fig. 2. The correlation between contact angle values and the flux for cleaned NF-DK virgin membrane.

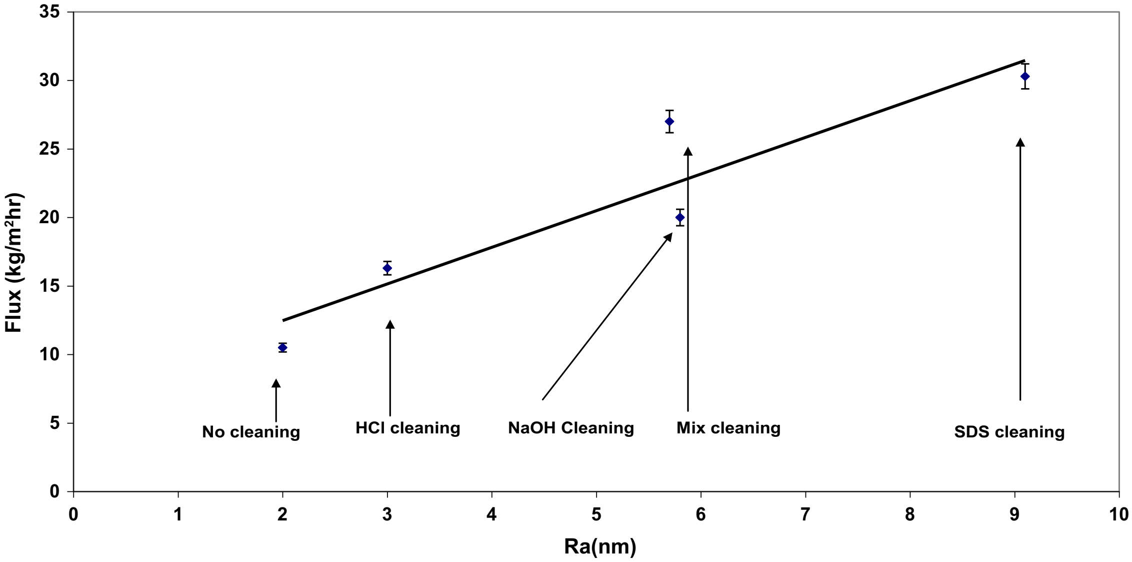

Fig. 3. The correlation between the flux and surface roughness values for virgin membranes cleaned by various cleaning agents. Note fouled membranes gave no flux.

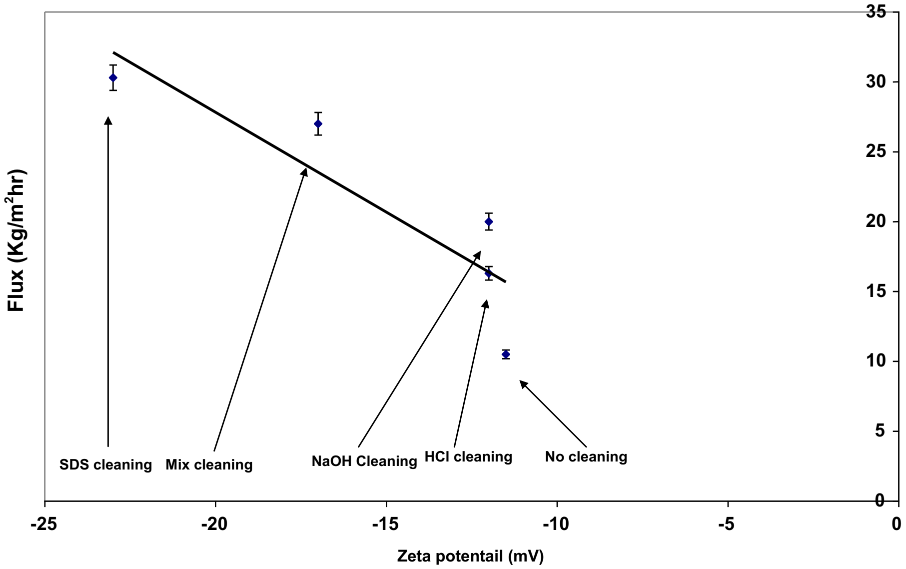

Fig. 4. Correlation between zeta potential and flux for virgin membrane cleaned by various cleaning agents.

The membrane flux increases as the membrane surface pore size becomes larger (Fig. 1). For example, the flux was increased for treated virgin membrane with HCl, NaOH, SDS, and mix to 9.2, 14.5, 16.1, and 17.6 kg/m^2 h, respectively, as the pore size was increased accordingly to 0.28, 0.29, 0.30, and 031 nm, respectively.

The correlations figures (see Figs. 2–4) between the flux and contact angle, zeta potential values, and surface roughness (AFM) have shown very positive results. The correlation result between contact angle values and the flux for cleaned virgin membranes shows that as the contact angle values increased the membrane flux decreased (Fig. 2). Decreasing contact angle values results in the membrane surface becoming more hydrophilic, and thus an increase in the flux. Therefore, cleaning efficiency could be evaluated by the contact angle/flux relationship for different chemical cleaning agent concentrations and operational conditions. There is also close correlation between surface roughness values with the flux for virgin membranes and then treated virgin membrane (Fig. 3). The results obtained reveal that the flux increases as the surface roughness values increase. Consequently, the cleaning efficiency could be evaluated by the surface roughness value with flux at various chemical and physical operation conditions. The result obtained from the correlation between zeta potential and flux for the NF membranes indicate that the zeta potential of these membranes conveys very useful information (Fig. 4). The membrane flux increases as the membrane surface becomes more negative as a result of cleaning agents adsorption. For example, when the membrane is cleaned with SDS, the membrane surface exhibited a higher negative charge than when compared with other membranes cleaned with other cleaning agents. Also, the membrane cleaned with SDS gave a greater flux than membranes cleaned with other cleaning agents.

The correlation results obtained from these techniques reveal that the rejection of the NF membrane for the SDS and the mix agent high-pH cleaning agent gave the lowest rejection of 88 and 92%, respectively (Fig. 5), revealing that the membrane surface

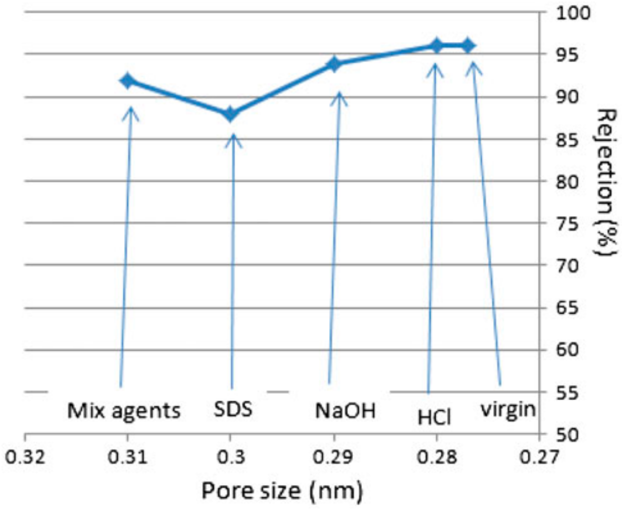

Fig. 5. The correlation between pore size and the rejection for virgin membrane cleaned by various cleaning agents.

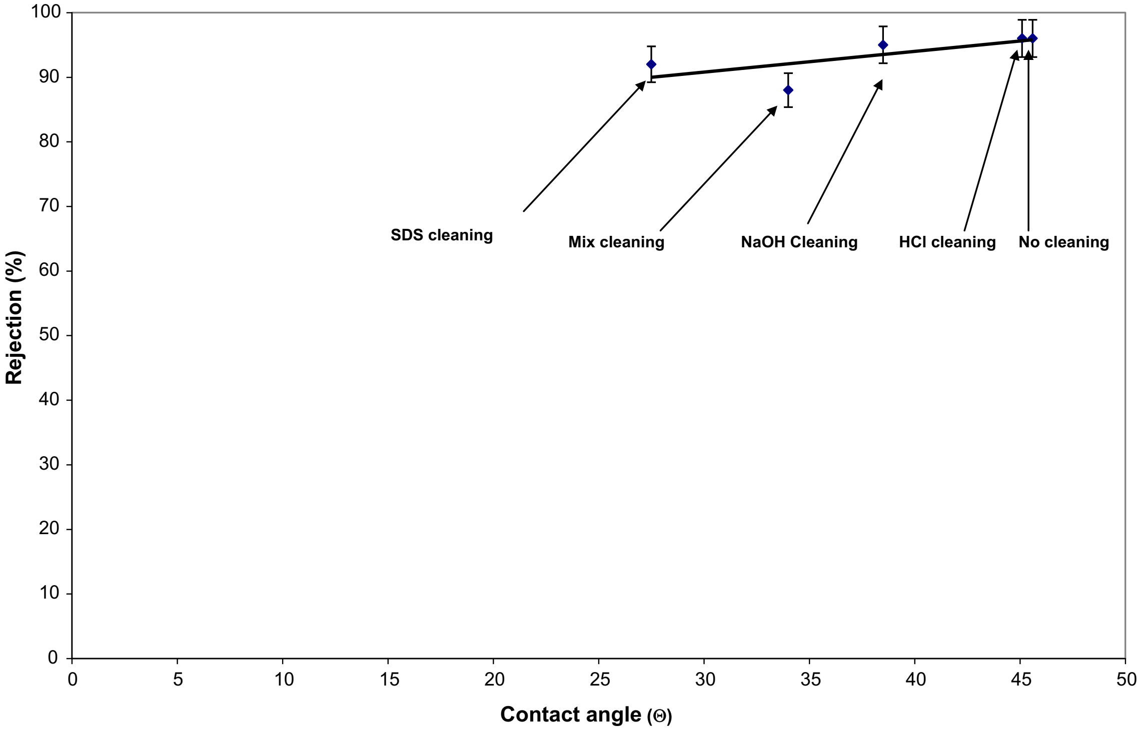

Fig. 6. The correlation between contact angle values and the rejection of divalent ions for cleaned NF DK virgin membranes.

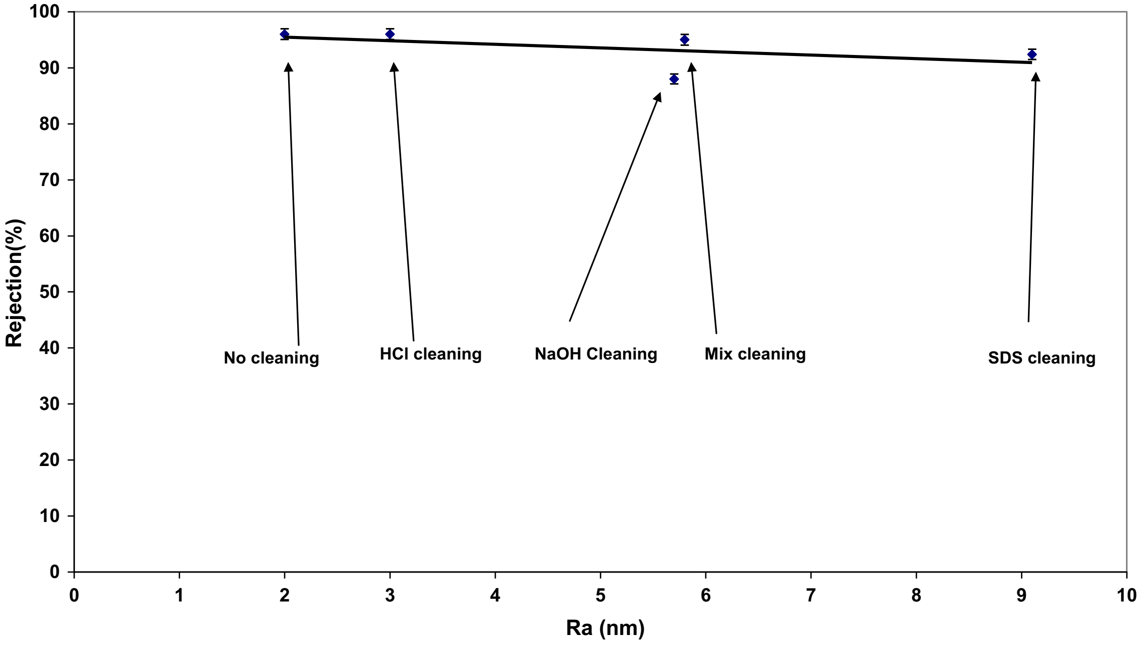

Fig. 7. The correlation between the rejection and surface roughness values for virgin membrane cleaned by various cleaning agents.

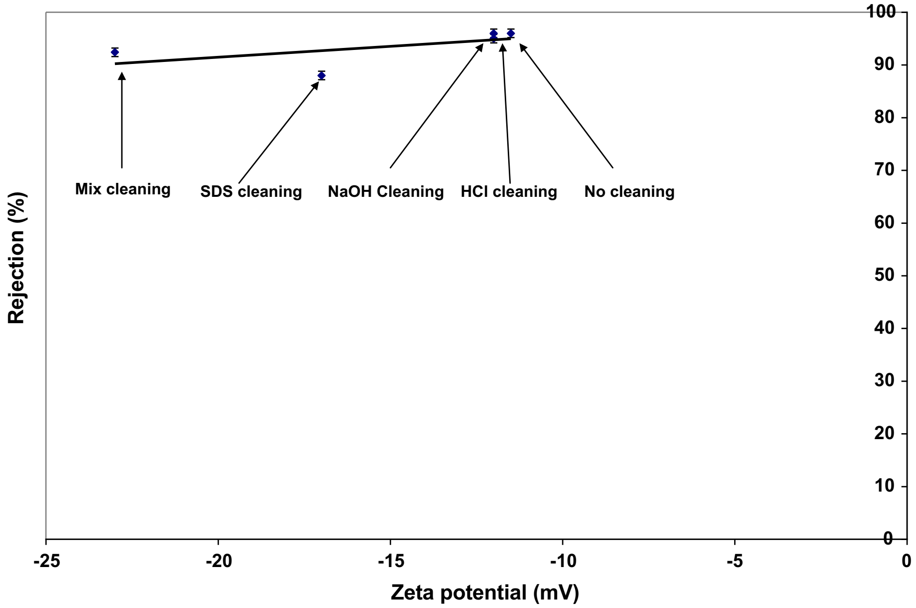

Fig. 8. The correlation between zeta potential and the rejection for virgin membrane cleaned by various cleaning agents.

properties, such as the pore size, have been strongly affected by this treatment when compared with other cleaning agents. This signifies a possible enlargement in membrane pore size and adsorption of the high-pH cleaning agents within the membrane surface or a degradation of the polymer in the active layer [22–24]. From the obtained result, the treated membrane with the low-pH cleaning agents had minor effect on the membrane surface properties when compared with high-pH cleaning agents [22–24]. The correlation of rejection of the hydrate magnesium sulfate with contact angle values, surface roughness, and zeta potential for untreated and treated virgin NF DK membrane reveals that the virgin membrane without any treatment shows the highest rejection when compared with the low- and high-pH cleaning agents (Figs. 6–8). The correlation results obtained from these techniques show that the rejection of the NF membrane cleaned with the low-pH cleaning agents were found to exhibit a similar value to the untreated virgin membrane. This shows that the low-pH cleaning agents did not have an adverse effect on the membrane surface properties compared with other high-pH cleaning agents. The correlation results obtained from these techniques reveal that the rejection of the NF membrane for the SDS high-pH cleaning agent gave the lowest rejection revealing that the membrane surface properties have been strongly affected by this treatment when compared with other high-pH cleaning agents. This signifies a possible adsorption of the high-pH cleaning agents within the membrane surface or a degradation of the polymer in the active layer [22–24].

4. Conclusion

The overall result from this work illustrates that the pore size, contact angle, surface roughness, and zeta potential measurements provide valuable information and details about the membrane surface state after cleaning processes and also it is a reliable technique to assess the surface state of cleaned NF membranes. Usually, chemical cleaning is found to modify membrane surface properties for both treated and untreated virgin membranes; however, the present study suggests that the cleaning does have a major effect on the performance of NF membranes and their surface properties.

The pore size measurements by positron annihilation spectroscopy indicate that mix and SDS cleaning agents had profound adverse effective on the virgin NF membranes. The membrane surface properties were modified to the extent where the pore size was increased over 12% indicating irreversible chemical reaction and adsorption at the membrane surface whereas, HCl cleaning resulted in pore size that is almost similar to that of virgin NF untreated membrane. The contact angle measurements indicate that mix and SDS cleaning agents had very adverse effective on both treated and untreated virgin membranes. The membrane surface properties were modified to the extent where the flux was increased over 100% and membrane hydrophilicity was increased significantly (low contact angle measurement) indicating irreversible chemical reaction and adsorption at the membrane surface. However, NaOH cleaning results revealed better performance with considerable cleaning efficiency whereas HCl cleaning resulted in poor cleaning efficiency. The surface roughness indicates that mix and SDS cleaning agents have adverse effects on both treated and untreated virgin membranes. However, NaOH cleaning results revealed improved performance with considerable cleaning efficiency while HCl cleaning resulted in poor cleaning efficiency. The zeta potential of all virgin membranes cleaned with SDS changed to more negative values across the pH range compare with untreated virgin TFM. The SDS readily adsorbs to the membrane surface and the negatively charged functional group of SDS dominate the membrane surface charge but the extent varies and depends on the reaction between the membrane and the cleaning agent concentrations.

The correlations data between the flux of pure water and contact angle values, surface roughness, zeta potential, and pore size have shown very positive results. Correlations are shown for both virgin and cleaned virgin membranes. The correlation result between contact angle values and the pure water flux for cleaned virgin membranes shows that as the contact angle values increased the membrane flux decreased. Decreasing contact angle values results in the membrane surface becoming more hydrophilic, and thus an increase in pure water flux. Therefore, cleaning efficiency could be evaluated by the contact angle/flux relationship for different chemical cleaning agent concentrations and operational conditions. There is also close correlation between surface roughness values with the flux for cleaned virgin membranes and then cleaned virgin membrane. The results obtained reveal that the flux increases as the surface roughness values increase. The result obtained from the correlation between zeta potential and flux for the different membranes indicate that the zeta potential of these membranes conveys very useful information. The membrane flux increases as the membrane surface becomes more negative as a result of cleaning agents adsorption.

The correlation between the rejection of $MgSO_4 \cdot 7H_2O$ with contact angle values, surface roughness, zeta potential, and pore size reveal that the data obtained from these techniques show that the rejection deteriorated with high-pH cleaning agents (SDS, mix, and NaOH) when compared with low-pH cleaning agents (HCl). This shows that the high-pH cleaning agents are not only adsorbed within the membrane surface but also deteriorates the active layer of membrane surface.

In general, all the techniques are providing very useful information about the membrane surface state that could help the researchers to identify the root cause of the problem and how they can be treated with less membrane deterioration.

Acknowledgment

We thank GE Osmonics for the donation of the virgin NF membrane (DK).

References

[1] A. Al-Amoudi, P. Williams, S. Mandale, R.W. Lovitt, Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability, Sep. Purif. Technol. 54(2) (2007) 234–240.10.1016/j.seppur.2006.09.014

[2] V. Mavrov, H. Chmiel, B. Heitele, F. Rögener, Desalination of surface water to industrial water with lower impact on the environment. Part 2: Improved feed water pretreatment, Desalination 110(1–2) (1997) 65–73.10.1016/S0011-9164(97)00085-4

[3] B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration, J. Membr. Sci. 156 (1999) 29–41.10.1016/S0376-7388(98)00326-3

[4] H. Lee, G. Amy, J. Cho, Y. Yoon, S. Moon, I.S. Kim, Cleaning strategies for flux recovery of an ultrafiltration membrane fouled by natural organic matter, Water Res. 35 (2001) 3301–3308.10.1016/S0043-1354(01)00063-X

[5] G. Morel, N. Ouazzani, A. Graciaa, J. Lachaise, Surfactant modified ultrafiltration for nitrate ion removal, J. Membr. Sci. 134 (1997) 47–57.10.1016/S0376-7388(97)00093-8

[6] J. Vrouwenvelder, J. Kappelhof, S. Heijrnan, J. Schippers, D. van der Kooija, Tools for fouling diagnosis of NF and RO membranes and assessment of the fouling potential of feed water, Desalination 157 (2003) 361–365.10.1016/S0011-9164(03)00417-X

[7] B. Van der Bruggen, L. Braeken, C. Vandecasteele, Flux decline in nanofiltration due to adsorption of organic compounds, Sep. Purif. Technol. 29(1) (2002) 23–31.10.1016/S1383-5866(01)00199-X

[8] S. Lee, J. Kim, C.-H. Lee, Analysis of $CaSO_4$ scale formation mechanism in various nanofiltration modules, J. Membr. Sci. 163(1) (1999) 63–74.10.1016/S0376-7388(99)00156-8

[9] A. Al-amoudi, Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: A review, Desalination 259 (2010) 1–10.10.1016/j.desal.2010.04.003

[10] H. Zhu, M. Nyström, Cleaning results characterized by flux, streaming potential and FTIR measurements, Colloids Surf., A 138(2–3) (1998) 309–321.10.1016/S0927-7757(97)00072-1

[11] B. Van der Bruggen, C. Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, Water Res. 36(5) (2002) 1360–1368.10.1016/S0043-1354(01)00318-9

[12] W.R. Bowen, A.W. Mohammad, N. Hilal, Characterisation of nanofiltration membranes for predictive purposes—Use of salts, uncharged solutes and atomic force microscopy, J. Membr. Sci. 126(1) (1997) 91–105.10.1016/S0376-7388(96)00276-1

[13] C. Labbez, P. Fievet, A. Szymczyk, A. Vidonne, A. Foissy, J. Pagetti, Analysis of the salt retention of a titania membrane using the "DSPM" model: Effect of pH, salt concentration and nature, J. Membr. Sci. 208 (1–2) (2002) 315–329.10.1016/S0376-7388(02)00310-1

[14] W.R. Bowen, T.A. Doneva, H.B. Yin, Polysulfone—sulfonated poly(ether ether) ketone blend membranes: Systematic synthesis and characterisation, J. Membr. Sci. 181 (2) (2001) 253–263.10.1016/S0376-7388(00)00541-X

[15] W.R. Bowen, J. Welfoot, Modelling the performance of membrane nanofiltration—Critical assessment and model development, Chem. Eng. Sci. 57 (2002) 1121.10.1016/S0009-2509(01)00413-4

[16] W.R. Bowen, J. Welfoot, P. Williams, Linearized transport model for nanofiltration: Development and assessment, AICHE 48 (2002) 760.10.1002/(ISSN)1547-5905

[17] A. Al-Amoudi, C. Wright, P. Williams, R.W. Lovitt, A. Al-Hobiab, Atomic force microscopy (AFM) analysis of cleaned and fouled nanofiltration membranes, Int. J. Nano Biomater. 2 (2009) 82–91.10.1504/IJNBM.2009.027700

[18] A. Al-amoudi, NF Nanofiltration Membrane Characterizations, in Chemical Engineering, Swansea University, Swansea, 2009, pp. 1–243.

[19] A.S. Al-Amoudi, A.M. Farooque, Performance, restoration and autopsy of NF membranes used in seawater pretreatment, Desalination 178 (2005) 261–271.10.1016/j.desal.2004.11.048

[20] W.R. Bowen, T.A. Doneva, H.-B. Yin, Separation of humic acid from a model surface water with PSU/SPEEK blend UF/NF membranes, J. Membr. Sci. 206 (1–2) (2002) 417–429.10.1016/S0376-7388(01)00786-4

[21] A. Al-Amoudi, P. Williams, A.S. Al-Hobaib, R.W. Lovitt, Cleaning results of new and fouled nanofiltration membrane characterized by contact angle, updated DSPM, flux and salts rejection, Appl. Surf. Sci. 254 (2008) 3983–3992.10.1016/j.apsusc.2007.12.052

[22] N.D. Lawrence, J.M. Perera, M. Iyer, M.W. Hickey, G. W. Stevens, The use of streaming potential measurements to study the fouling and cleaning of ultrafiltration membranes, Sep. Purif. Technol. 48(2) (2006) 106–112.10.1016/j.seppur.2005.07.009

[23] W.S. Ang, S. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes, J. Membr. Sci. 272(1–2) (2006) 198–210.10.1016/j.memsci.2005.07.035

[24] Q. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: Measurements and mechanisms, Environ. Sci. Technol. 38(17) (2004) 4683–4693.10.1021/es0354162