Desalination and Water Treatment
www.deswater.com

10 (2009) 298–305

Surface modification of nanofiltration membrane for reduction of membrane fouling

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Received 15 September 2008; Accepted in revised form 27 August 2009

ABSTRACT

Membrane fouling is a major drawback to any membrane system. Fouling reduces the membrane flux either temporarily or permanently. Unfortunately, it is impossible to produce zero-fouling membranes but minimization of membrane fouling can be done efficiently. Membrane surface modification is one of the most often used methods to increase membrane resistance to fouling. The three major parameters that affect the membrane fouling are hydrophilicity, surface charge and surface roughness. Besides that, some researchers also suggest that two other parameters which should be taken into account are chemical composition and porosity. In this study, the first three major parameters mentioned above only are considered as contributing to fouling. Usually, these three parameters are characterized by three different techniques (hydrophilicity by contact angle measurement, surface roughness by atomic force microscopy (AFM) and surface charge by zeta potential). This study concentrates on characterising effect of surface roughness alone. Commercial polyethersulfone (PES) nanofiltration membranes with and without surface modification were characterized and humic acid was chosen as the foulants.

Keywords: Fouling; Nanofiltration; Surface modification; AFM

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1. Introduction

Nanofiltration membrane technology has been increasingly used in many applications especially in treatment of water and wastewater. However, fouling is a major problem for efficient use of nanofiltration (NF) membranes causes significant loss of productivity, product quality and added operational cost [1].

For membrane processes especially nanofiltration, the major problem is the permeate flux decline due to membrane surface fouling and concentration polarization [2,3]. Indirectly, this limitation affects the overall membrane performance and economics as well [4–6].

Fouling reduces the membrane flux either temporarily or permanently. Membrane fouling can be categorised as reversible or irreversible depending on the types of fouling and whether the flux reduction is temporary or permanent. Membrane fouling is considered reversible when flux recovery can be achieved by fluid dynamics or chemical cleaning and irreversible when flux decline cannot be fully recovered or flux recovery is not possible [7,8].

Pretreatments such as coagulation or flocculation or low pressure membrane filtration normally applied to reduce fouling. However fouling caused by small col-

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loid, biological macromolecules, dissolved organics and soluble salts may still block many RO and NF applications [9,10].

Reversible fouling can be treated by employing feed pretreatment, modifying the membrane surface or by membrane cleaning procedures. Zhang et al. [11] suggested membrane fouling can be reduced by changing regimes across the membrane surface, regular cleaning and changing the surface-foulant affinity (membrane – surface modifications).

Generally, in order to reduce the fouling problem, there are several approaches can be distinguished as proposed by Fane et al. [12]:

i) pretreatment of the feed solution,
ii) module and process conditions,
iii) cleaning procedures and iv) membrane properties.

Altering membrane properties, besides other fouling control methods, can directly lead to optimized systems with minimized fouling and effective cleaning [13].

Besides the bulk modification of polymers, surface modification of membranes is a promising approach to provide membranes with tailor-made separation properties and a reduced tendency for fouling [14]. Membrane properties have been investigated by many researchers in order to reduce fouling. These methods include radical polymerization [15,16], low temperature plasma [17,18] and photochemical [19,20] techniques. Photochemical grafting (especially UV-initiated grafting) techniques are widely used due to their low cost of operation, mild reaction conditions, selectivity to absorb UV light without affecting the bulk polymer and a possibility of easy incorporation into the end stages of a membrane manufacturing process [20]. Before surface modification can be done, characteristics of foulants should be considered as the foulants properties may also influence membrane performance.

Humic acid (HA) is one of the natural organic matters (NOM) which are a major fouling problem in the purification of surface water. Humic acids are expected to a result from condensation polymerisation reactions, amino acid sugar interactions, lignin biodegradation, and animal and plant decomposition [21]. However concentrations of humic acid in surface waters are heavily affected by changes in the weather [22]. HA is a heterogeneous mixture having both aromatic and aliphatic components [19] and contain three main functional groups: carboxylic acids (COOH), phenolic alcohol (OH) and methoxy carbonyl (C=O) [23]. Carboxylic functional groups account for 60–90% of all functional groups [24]. As a result, at the pH range of natural waters or at neutral to high pH, humic substances become negatively charged [25–27]. Humic acid is also more hydrophobic generally than other humic substances (e.g. fulvic acid) [28].

Humic acids are classified as dissolved organic carbon (DOC) and have an impact on water colour for concentrations above 5 mg/L [29]. Most countries have regulations for HA content in drinking water. For example, in New Zealand, the concentration of HA for reliable potable drinking water must be below the regulatory limit of 1.17 mg/L [22].

To attempt to reduce fouling by HA, a commercial nanofiltration membrane was modified by UV-irradiated grafting method. When modifying membrane surface, attention was given to the three major parameters that affect the membrane fouling: hydrophilicity, surface charge and surface roughness. Solute-membrane interactions are usually influenced by surface charge and hydrophilicity since solutes are often charged and have hydrophobic/hydrophilic characteristics. However, in this study this interaction was characterized by AFM alone in term of adhesion forces instead of using contact angle measurement (for hydrophilicity) and streaming potential (for surface charge). AFM was also used to characterize membrane surface morphology (roughness).

2. Experimental

2.1. Materials

Commercially available polyethersulfone nanofiltration flat sheet membrane (NFPES10, Nadir, Germany) was used for photochemical modification. Before use, the membranes were rinsed with de-ionized water to remove the wetting agent. Humic acid was provided by Aldrich and Acrylic Acid (AA)(99.5%) was obtained from Acros Organic.

2.2. Preparation of modified membrane

A membrane sample with a diameter of 5 cm was immersed in 5 g/L AA solution for 30 min. Next, the membrane was irradiated with ultraviolet light using a B-100 lamp (Ultra-Violet Products Ltd.) of relative radiation intensity of 21.7 mW/cm^2 at a wavelength of 350 nm for different exposure times to induce polymerization of AA on the membrane sample. After polymerization, membrane was rinsed intensively with water/methanol solution at room temperature to remove any non-grafted polymer and stored in de-ionized water overnight. The unmodified membrane was marked as 0 min UV time (the membrane was not immersed in the acrylic acid solution).

2.3. Nanofiltration procedure and solution analysis

Water permeability and solution flux experiments were performed using a cross-flow filtration system containing flat sheet membrane with a cell diameter of 7.5 cm. A circular disc membrane with an effective membrane area of 12.6 cm^2 was used in the current work. A gear pump with a variable speed was used to circulate the feed through the cell. The trans-membrane pressure and flow rate were adjusted using the retentate outlet valve and variable speed key of the pump. In all experiments, the membranes were immersed in de-ionized water overnight. Each membrane was pressurized at 10 bar for 30 min to avoid any compaction effects and to establish leak tightness. A water permeability test was performed with water produced by an ultrapure water system, Milli-Q, Millipore. A 15 mg/L solution of humic acid was prepared by dissolving humic acid powder in de-ionized water and the solution was adjusted to pH 10 with 1 M NaOH to make sure all the humic acid powder was completely dissolved. For fouling experiments, the same solution was adjusted to pH 7 by using 1 M HCl. In this study, the solution was circulated through the filtration system unit at constant pressure of 7 bar and a cross flow velocity of 0.3 m/s and permeate was collected and measured with an electronic balance. This feed solution was circulated under these conditions for 4 h to study the flux reduction over time. The experiment was conducted two times to get a reproducibility of the data.

For solution concentration measurements, a UV Absorbance Spectrophotometer (UV Mini-1240, Shimadzu) was used at a wavelength of 254 nm with Hellma 10 mm cell made of Quartz SUPRASIL. To measure unknown sample concentration, a standard calibration curve of absorbance against humic acid concentration (0–15 mg/L) was produced.

2.4. Atomic force microscopy (AFM)

A Mulitmode AFM (Veeco Instruments (USA)) was used to visualize membrane surfaces and to characterize the surface forces between the membrane and foulant. To quantify adhesion forces, a colloid probe was prepared which consisted of a silica glass sphere (Polysciences, Inc.) coated with a layer of HA. Details of force measurement acquisition are described elsewhere [20,30]. The AFM cantilevers used had their force constants measured by the static deflection method [31].

3. Results and discussion

3.1. Permeability and flux reduction

Membrane permeability for unmodified and modified membranes was measured at room temperature and the result is shown in Fig. 1. UV irradiation had a significant effect on clean water permeability. This shows that the base membrane (NFPES10) characteristics changed because the membrane surface was grafted with acrylic monomers during the UV irradiation process. The water permeability for all modified membranes was higher than unmodified membrane. As can be seen in Fig. 1, as the irradiation time increased, the water permeability increased more than 1.5 times for membrane irradiated with 1 and 3 min, however this value starts decreasing after 5 min of irradiation time which is near to value of unmodified membrane.

This situation could be explained by hydrophilic characteristics of membrane surfaces. Roudman and DiGiano [25] showed that increasing hydrophilicity leads to the formation of hydrophilic channels or highways which increase the rate of water permeation. In this study, by increasing the irradiation time, more acrylic monomers were incorporated onto the membrane surface. Increasing the amount of acrylic acid grafted on the membrane surface will indirectly increase the membrane hydrophilicity [32–34] and these membrane properties will have influenced the water permeability of the membrane. This is consistent with studies by Qiu et al. [32], where it was found that the degree of grafting of acrylic monomers increased and the contact angle was decreased (hydrophilicity increased) when the irradiation time increased. The same pattern was also observed by Kilduff et al. [35], where the modification of NFPES10 with N-vinyl-2-pyrrolidinone (NVP) decreased the contact angle as irradiation time was increased.

For membrane with 5 min irradiation time, the lower water permeability compared to the other two modified

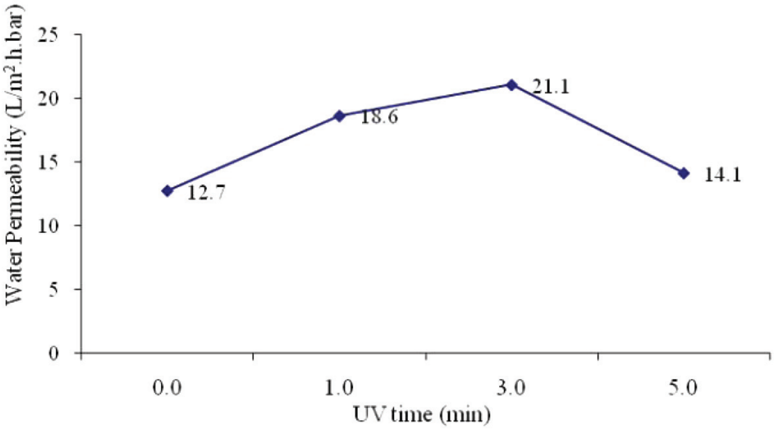

Fig. 1. The effects of UV exposure time on pure water permeability.

membranes could be due to the acrylic monomer grafted on the membrane surface started constricting pores, blocking the membrane pores or both.

The humic acid solution was circulated through the membrane system for 4 h (240 min) at a constant pressure of 7 bar. Filtration of humic acid solution (Fig. 2) shows that the initial permeation rate for all modified membranes decreased with increasing UV irradiation time. As the irradiation time was increased, more acrylic monomer would have grafted on membrane surface increasing the charge density. Carroll et al. [33] used acrylic acid monomer to produce negatively charged surface on polypropylene hollow-fiber microfiltration membrane. The interactions between the negative fixed charges of grafted acrylic polymer on the membrane surface and the negatively charged humic acid at pH 7 increase hydraulic resistance, contributing significantly to the lower initial permeation rate in order of irradiation time of 5 min < 3 min < 1 min.

In order to interpret the fouling behaviour of the membrane, the data were normalized relative to initial flux values (Fig. 3). The tendency of the NFPES10 nanofiltration membrane to foul was reduced by UV for all irradiation times or in other words the acrylic grafted membrane has the ability to increase resistance to membrane fouling. After 4 h of operation, the unmodified membrane shows the highest flux reduction compared to modified membrane with a 26% reduction of initial permeate flux. All the modified membranes were less prone to fouling than unmodified and membrane irradiated at 5 min had the most stable flux over the operation time, without showing a significant flux reduction (5 % flux reduction over 4 h operation). This could be explained by the negative charge density of the irradiated membrane being high enough to exclude/repel the humic acid solute from attaching to the membrane surface. The more important fact is that although all the modified membrane has different permeation rates, they still maintain a reasonable high rejection of humic acid as low as unmodified membrane (Table 1). There is no significant change in removal of humic acid over the 4 h of operation time.

Table 1
Rejection of 15 mg/L humic acid solution at 7 bar and pH 7 for different irradiation times at different operation time

Irradiation time (min)	Rejection (%) at different operation time*			
	1 h	2 h	3 h	4 h
0 (unmodified)	99	98	98	99
1	99	99	99	99
3	100	100	100	100
5	99	98	98	98

*error in concentration measurement and calculated rejection is less than 5%

3.2. AFM analysis

To get a better understanding of the role of membrane surface properties and fouling, AFM was used to visualize both modified and unmodified NFPES10 membrane. Figs. 4–7 show the three dimensional AFM images for initial and modified membranes, with scanning areas of 5 µm × 5 µm.

The roughness of the membrane surfaces was monitored by assessing three parameters, root mean square roughness (RMS), basically the standard deviation of the height values for all of the pixels in the image; the roughness average (R_a) an arithmetical mean of the absolute height values; and R_{max} the maximum range in heights on the image. Analysis of the surface morphology of the membranes have shown that the values of root mean square surface roughness (RMS) were increased with

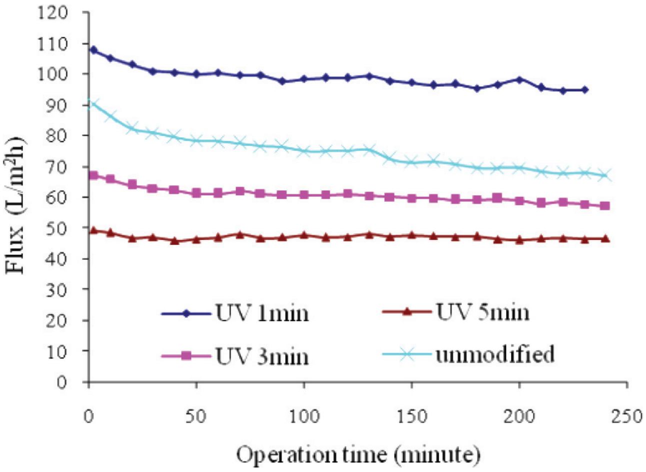

Fig. 2. Flux reduction of 15 mg/L humic acid solution during 4 h of operation at 7 bar and pH 7.

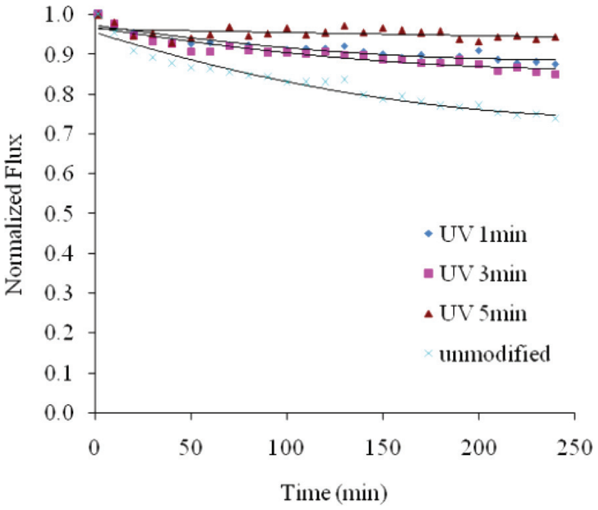

Fig. 3. Normalized flux of 15 mg/L humic acid solution during 4 h operation at 7 bar and pH 7.

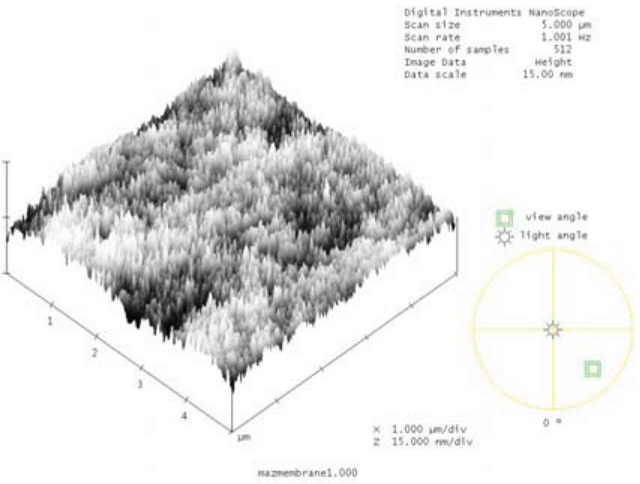

Fig. 4. High resolution 3D image of unmodified NFPES10 membrane.

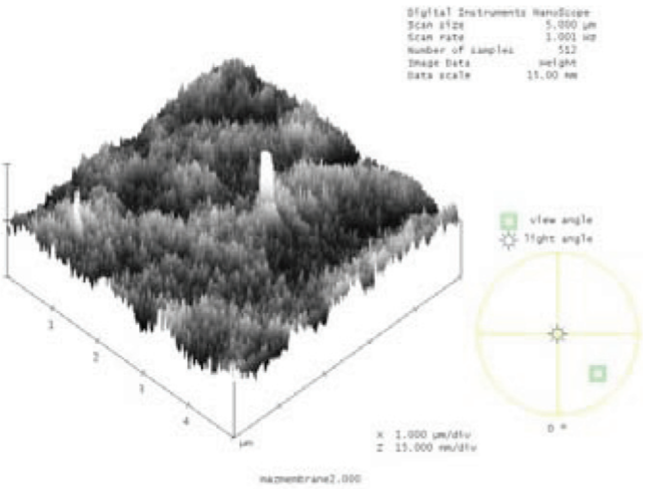

Fig. 5. High resolution 3D image of modified NFPES10 with 1 min irradiation.

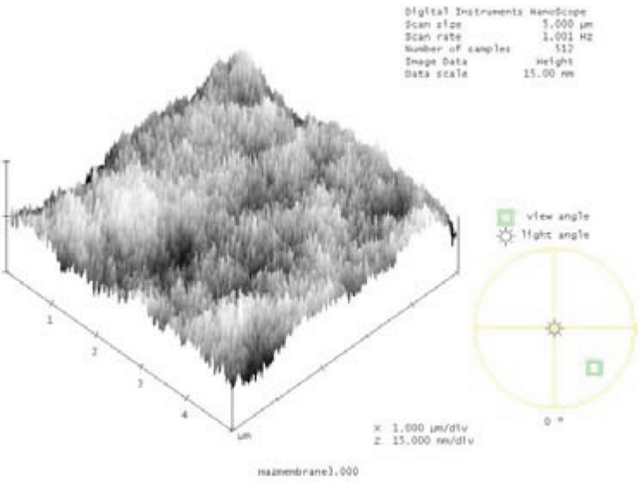

Fig. 6. High resolution 3D image of modified NFPES10 with 3 min irradiation.

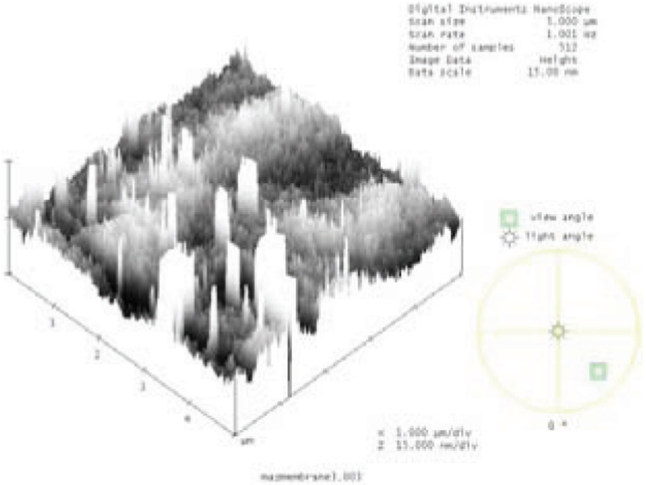

Fig. 7. High resolution 3D image of modified NFPES10 with 5 min irradiation.

increasing irradiation time and 5 min irradiation showed the roughest surface among all the membranes with an almost 3 fold increase in the RMS roughness compared to unmodified membrane (Table 2). It seems that our assumption that the highest amount of grafted acrylic monomer on the membranes surface occurs with 5 min irradiation would be reasonable.

As well as hydrophility, the, increase in surface roughness of the modified membrane could be one of the factors affecting water permeability compared to the unmodified membrane. Studies by Hirose et al. [36] on cross-linked aromatic polyamide composite reverse osmosis (RO), found an approximately linear relationship between surface roughnesses and flux where they observed that an increase in surface roughness produced a very high flux due to the increasing of the effective membrane area.

Membrane surface roughness is one of the most controversial issues due to its effect on flux and fouling. On the other hand, according to Vrijenhoek et al. [37], colloidal (silica particles with 0.1 µm diameter) fouling can be correlated with surface roughness of nanofiltration membrane. Their experiments showed that the permeate flux for the rougher composite polyamide membranes was substantially lower than the permeate flux of cellulose acetate with smoother surface. Colloidal particles preferentially accumulated at the valleys of rough membrane surface and blocking the valleys, resulting in a more severe flux reduction. This contrast with what we found

Table 2
Measurement of roughness parameters with contact mode from AFM images

Irradiation time	RMS (nm)	R_a (nm)	R_{max} (nm)
0 (unmodified)	1.621	1.280	16.585
1	1.823	1.401	50.880
3	1.988	1.559	29.116
5	4.699	2.456	103.91

in this study where the roughest membrane showed the lowest flux reduction. This could be explained by the characteristic of the foulants itself as mentioned by Hong and Elimelech [26]. In this study, was undertaken at high pH, low ionic strength and absence of divalent cations, humic acid in solution is in a stretched and linear configuration, hence roughness would not have a significant effect on flux decline.

Interaction of solutes is normally characterized by membrane properties through membrane hydrophilicity/hydrophobicity and membrane fixed charge using contact angle measurement and streaming potential respectively. However in this study, AFM was used to characterise membrane properties in terms of the force of adhesion using a HA coated silica probe, as shown in Fig. 8. A typical force measurement between the colloid probe and the membrane surface is presented in Fig. 9. Force measurements were carried out at 5 different locations on the surface, to minimise effects of localised surface geometry. Full explanation of AFM force-distance curves are described in detail elsewhere [20].

Adhesion forces vs. the degree of membrane treatment are shown in Fig. 10. Measurement with HA coated-silica probe showed a very good agreement with the experimental hypothesis. At a loading force of 15 nN, when HA-coated silica colloid probe was retracted from the membrane surface the adhesion force was much higher for the unmodified membrane compared to all modified membranes. This trend was also observed previously [20] where they found a higher adhesion force for initial ultrafiltration PES membrane compared to modified membrane. Membrane with 3 min and 5 min irradiation times demonstrated the lowest measured adhesion forces indicating that they have a higher resistance to fouling than less modified or unmodified membranes. This could be due to the more negatively charged surface on the grafted membrane being strong enough to repel/exclude the negative charge of humic acid, with a resultant decrease in the adhesion force. This is consistent with the

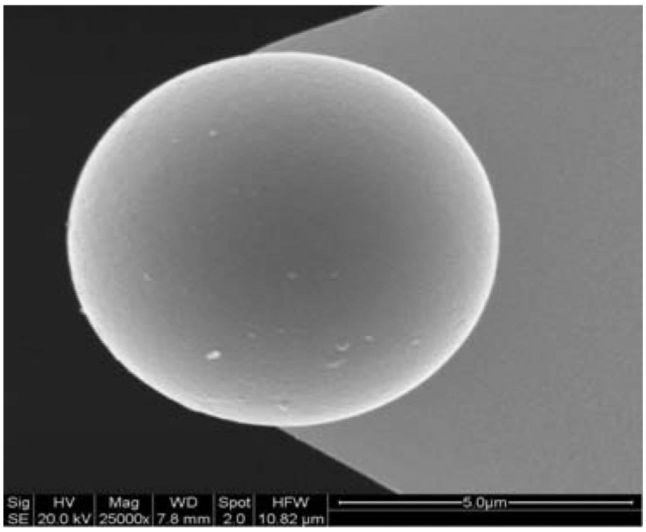

Fig. 8. Scanning electron microscope image of HA coated-silica probe.

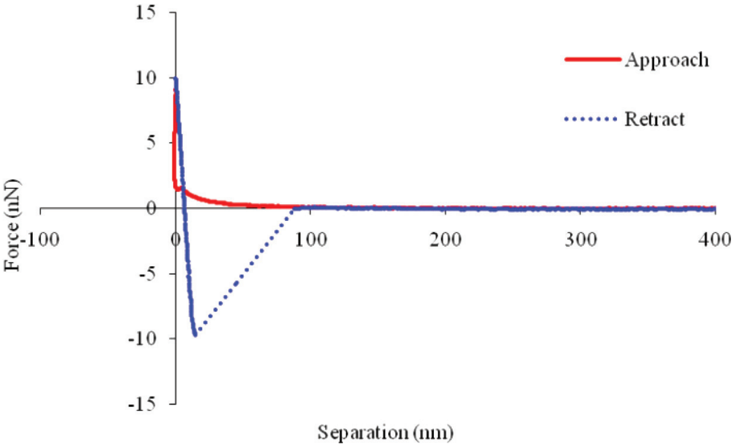

Fig. 9. Example force versus distance measurement between a silica probe and membrane surface. Attractive forces are negative. Magnitude of the maximum attractive force reached on the retract curve (------) gives the adhesion value for this curve.

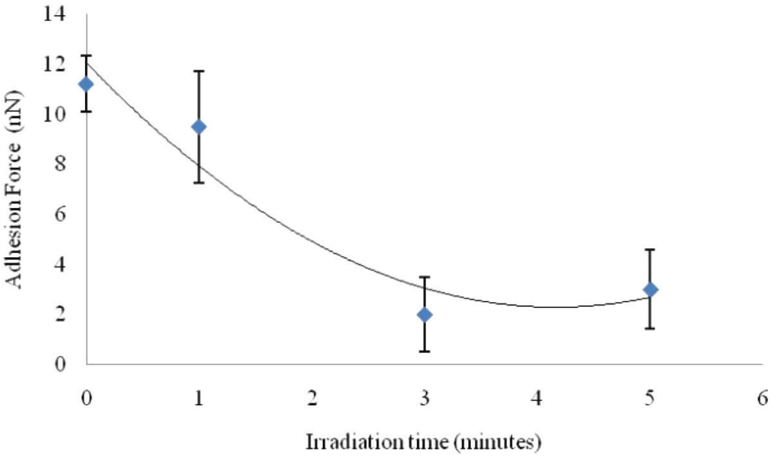

Fig. 10. Adhesion force for unmodified and grafted membrane at 15 nN loading force in pure water.

previous assumption, based on experimental data, that the modified membrane is more resistant to fouling than the unmodified membrane.

4. Conclusion

NFPES10 nanofiltration membranes were surface modified by using UV-initiated grafting technique with acrylic acid as monomer at different time of polymerization. All modified membranes have shown a very good tendency for reducing fouling compared to unmodified membrane with the higher degree of modification has the higher resistant to be fouled. This is supported not only by the fouling experimental data, but also from the adhesion force measured using AFM.

References

[1] C.Y. Tang, Y.N. Kwon and J.O. Leckie, Fouling of reverse osmosis and nanofiltration membranes by humic acid — Effects of solution composition and hydrodynamic conditions. J. Membr. Sci., 290 (2007) 86–94.

[2] A. Morao, I.C. Escobar, M.T. Pessoa de Amorim, A. Lopes and I.C. Goncalves, Postsynthesis modification of a cellulose acetate ultrafiltration membrane for applications in water and wastewater treatment. Environ.l Progress, 24(4) (2005) 367–382.

[3] S.C. Tu, V. Ravindran, D. Walter and M. Pirbazari, Predictive membrane transport model for nanofiltration processes in water treatment. AIChE J., 47(2) (2001) 1346–1362.

[4] G.B. Van den Berg and C.A. Smolders, Flux decline in membrane processes. Filtr. Separ., 25 (1988) 115.

[5] M. Pirbazari, B.N. Badriyha and V. Ravindran, MF-PAC for treating waters contaminated with natural and synthetic organics. J. AWWA, 84(2) (1992) 95.

[6] J. Mallevialle, P.E. Odendaal and M.R. Wiesner, Water Treatment Membrane Processes. McGraw-Hill, New York, 1996.

[7] S. Chellam and M.R. Wiesner, Particle transport in clean membrane filters in laminar flow, Environ. Sci. Technol., 26 (1992) 1611

[8] H. Shimizu, H. Katakami and S. Nagaoka, Membrane formation mechanism and permeation properties of a novel porous polyimide membrane. Polymers Adv. Technol., 13 (2002) 370–380.

[9] E.M.V. Hoek and M. Elimelech, Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes. Environ. Sci. Technol., 37 (2003) 5581–5588.

[10] Q. Li and M. Elimelech, Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter. J. Membr. Sci., 278 (2006) 72–82.

[11] L. Zhang, G. Chowdhury, C. Feng, T. Matsuura and R. Narbaitz, Effect of surface -modifying macromolecules and membrane morphology on fouling of polyethersulfone ultrafiltration membrane. J. Appl. Polymer Sci., 88 (2003) 3132–3138.

[12] A.G. Fane, P. Beatson and H. Li, Membrane fouling and its control in environmental applications. Water Sci. Technol., 41 (10–11) (2000) 303–308.

[13] A. Al-Amoudi and R.W. Lovitt, Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. J. Membr. Sci., 303 (2007) 4–28.

[14] J.A. Koehler, M. Ulbricht and G. Belfort, Intermolecular forces between proteins and polymer films with relevance to filtration, Langmuir, 13(15) (1997) 4162–4171.

[15] A. Asatekin, A. Menniti, S. Kang, M. Elimelech, E. Morgentroth and A.M. Mayes, Antifouling nanofiltration membranes for membrane bioreactors from self-assembling graft copolymers. J. Membr. Sci., 285 (2006) 81–89.

[16] S. Belfer, J. Gilron, Y. Purinson, R. Fainshtain, N. Daltrophe, M. Priel, B. Tenzer and A. Toma, Effect of surface modification in preventing fouling of commercial SWRO membranes at the Eilat seawater desalination pilot plant. Desalination, 139 (2001) 169–176.

[17] A.K.S. Ang, E.T. Kang, K.G. Neaoh, K.L. Tan, C.Q. Cui and T.B. Lim, Low-temperature graft copolymerization of 1-vinyl imidazole on polyamide films simultaneous lamination to copper foils-effect of crosslinking agents. Polymer 41 (2000) 489–498.

[18] H. Chen and G. Belfort, Surface modification of poly(ether sulfone) ultrafiltration membranes by low-temperature plasma-induced graft polymerization. J. Appl. Polymer Sci., 72 (1999) 1699–1711.

[19] H. Susanto and M. Ulbricht, High-performance thin-layer hydrogel composite membranes for ultrafiltration of natural organic matter. Water Res., 42 (2008) 2827–2835.

[20] N. Hilal, L. Al-Khatib, B.P. Atkin, V. Kochkodan and N. Potapchenko, Photochemical modification of membrane surfaces for (bio)fouling reduction: a nano-scale study using AFM. Desalination, 158 (2003) 65–72.

[21] A.I. Schafer, Natural Organic Removal Using Membrane: Principles, Performance and Cost. Technomic Publishing Co., Pennsylvania, USA, 2001.

[22] J. Lowe and M.M. Hossain, Application of ultrafiltration membranes for removal of humic acid from drinking water. Desalination, 218 (2008) 343–354.

[23] Y. Wei and A.L. Zydney, Humic acid fouling during microfiltration. J. Membr. Sci., 157 (1999) 1–12.

[24] G.R. Aiken, D.M. McKnight, R.L. Wershaw and P. MacCarthy, Humic Substances in Soil, Sediment and Water, Wiley, New York, 1985.

[25] A.R. Roudman and F.A. DiGiano, Surface energy of experimental and commercial nanofiltration membranes: effects of wetting and natural organic matter fouling. J. Membr. Sci., 175 (2000) 61–73.

[26] S. Hong and M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. J. Membr. Sci., 132 (1997) 159–181.

[27] C. Combe, E. Molis, P. Lucas, R Riley and M.M. Clark, The effect of CA membrane properties on adsorptive fouling by humic acid. J. Membr. Sci., 154 (1999) 73–87.

[28] C. Jucker and M.M. Clark, Adsorption of aquatic humic substances on hydrophobic ultrafltration. J. Membr. Sci., 97 (1994) 37–52.

[29] A.I. Schafer, A.G. Fane and T.D. Waite, Fouling effects on rejection in the membrane filtration of natural waters. Desalination, 131 (2000) 215–224.

[30] N. Hilal, W.R. Bowen, L. Al-Khatib and O. Ogunbiyi, A review of atomic force microscopy applied to cell interactions with membranes. Trans. IChemE, Part A: Chem. Eng. Res. Design, 84(A4) (2006) 282–292.

[31] C.T. Gibson, G.S. Watson and S. Myra, Determination of the spring constants for force microscopy/spectroscopy. Nanotechnol., 7 (1996) 259–262.

[32] C. Qiu, Q.T. Nguyen and Z. Ping, Surface modification of cardo polyetherketone ultrafiltration membrane by photo-grafted copolymers to obtain nanofiltration membranes. J. Membr. Sci., 295 (2007) 88–94.

[33] T. Caroll, N.A. Booker and J. Meier-Haack, Polyelectrolyte-grafted microfiltration membranes to control fouling by natural organic matter in drinking water. J. Membr. Sci., 203 (2002) 3–13.

[34] M. Taniguchi, J.E. Kilduff and G. Belfort, Low fouling synthetic membranes by UV-assisted graft polymerization: monomer selection to mitigate fouling by natural organic matter. J. Membr. Sci., 222 (2003) 59–70.

[35] J.E. Kilduff, S. Mattaraj, J.P. Pieracci and G. Belfort, Photochemical modification of poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes for control of fouling by natural organic matter. Desalination, 132 (2000) 133–142.

[36] M. Hirose, H. Ito and Y. Kamiyama, Effect of skin layer surface structures on the flux behaviour of RO membranes. J. Membr. Sci., 121 (1996) 209.

[37] E.M. Vrijenhoek, S. Hong and M. Elimelech, Influence of membrane properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. J. Membr. Sci., 188 (2001) 115–128.