Enhanced Filtration Characteristics and Reduced Bacterial Attachment for RO Membranes Modified by a Facile Method

Supporting Information

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1 Experimental

1.1 Materials

Commercial reverse osmosis (RO) membranes (UTC-80LB from Toray, Inc.) were purchased from Sterlitech Corporation, Kent, Washington WA 98032. Table 1 gives the details of the performance of the membranes from tests performed using feedwater of NaCl concentration (35g/L) at 25 ^{o}C and a pressure of 55 bars (800 psi). The reagents and chemicals used in this study include; N-(6-aminohexyl)-aminomethyltriethoxysilane, 3-(aminopropyl)triethoxysilane, ethylene glycol (EG), ethyl iodide (EtI) (procured from Sigma Aldrich),, absolute ethanol (EtOH), potassium persulfate ($K_2S_2O_8$), and sodium pyrosulfate ($Na_2S_2O_5$) (Fluka chemicals), and hydrochloric acid, HCl (from Fisher Scientific). All these chemicals and reagents were of pure standards and used without further purification. All solutions were prepared using ultrapure

deionized water. The molecular structure for both silanes is shown in Figure S1. The major differences are in the length of the main alkyl chain as well as the number of amine groups.

Figure S1 The molecular structure of the two silanes depicting the similarities and contrasts between them (a) N-(6-aminohexyl)-aminomethyltriethoxysilane with 2 amine groups (b) 3-(aminopropyl)triethoxysilane with the lone terminal group.

Table S1: Manufacturer data sheet for the performance of the membrane used in this study

Manufacturer	**Polymer**	**Code**	**Rejection (%)**	**Test pressure**	**Flux (L/m^{2}h)**
Toray	Polyamide	UTC-80LB	99.8	55 bar	46

1.2 Film deposition

The deposition of the films on the membrane was exactly as reported by Kim *et al.*[1] with minor changes. The commercial RO membrane sheets were cut into the sizes of 5cm by 5cm, cleaned with deionized water, and then submerged into 5% weight/volume of glycol for 30 minutes. Drying of the membranes took place at about 70^{o}C in a vacuum oven. This was followed by etching of the membranes in a solution of 0.01M $K_2S_2O_8$ and 0.01M $Na_2S_2O_5$ in the ratio of 1:1 for 30 minutes and then rinsing with deionized water to remove loosely bonded polyamide layers. To prepare the silane coupling solution (sol), *N-(6-aminohexyl)-aminomethyltriethoxysilane* and *3-*

(aminopropyl)-triethoxysilane were added independently to absolute ethanol (EtOH) in the ratios of 1:1 into a round-bottomed flask. This was followed by 16 ml of deionized water and few drops of concentrated hydrochloric acid. These were kept stirring for 60 minutes at 60 ^{o}C. These solutions were later transferred to an open flask and the etched membranes immersed and allowed to stand for 1 h (gelation). Thereafter, the membrane was removed, rinsed severally with deionized water and cured at 70 ^{o}C in a vacuum oven for 10 minutes.

1.3 Quaternization

Quaternization (introduction of positive charge on the N atoms) of the silane molecules occurred after the molecules had been deposited on the membrane surface. It involved the replacement of the hydrogen atoms of the amine groups of the silane molecule by alkyl groups. The silane coupled membranes were dipped in an aqueous solution containing 4% (V/V) Ethyl Iodide and Ethanol for 1 hr. This was followed by rinsing with deionized water and curing at 70 ^{o}C in a vacuum oven for 10 min. The entire steps of the quaternization are shown in Fig. 1. The thickness of the silane coating under the above reaction conditions is expected to be in the range 5 – 10 nm.

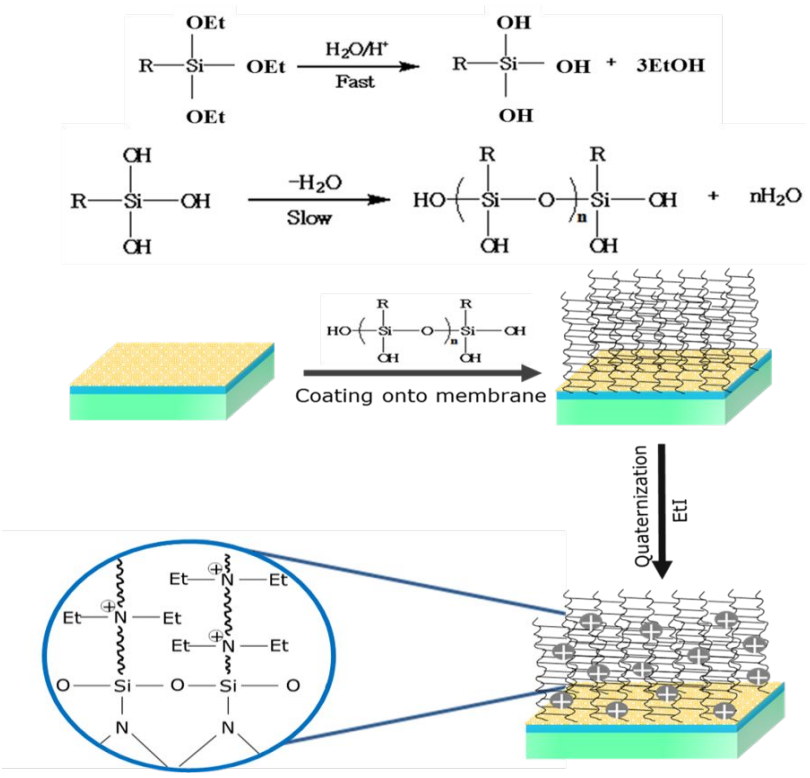


Figure S2 A schematic sketch and chemical reactions depicting the silane deposition and the subsequent quaternization on the membrane surface. Hydrolysis and condensation of the silane groups to form silanols (Si-OH) take place first, followed by the siloxane (Si-O-Si) groups. The silane film-membrane bond occurs through the Si-N bonds with N atoms of the polyamide. Quaternization results in replacement of an H atom by alkyl groups endowing a positive charge to the N.

Sample coding: 3-APS C = coated with 3-APS only; 6-AHAS C = coated with 6-AHAS only; 3-APS C&Q = coated with 3-APS and quaternized, 6-AHAS C&Q = coated with 6-AHAS and quaternized

1.4 Membrane characterization

Field-emission scanning electron microscope (FESEM, LYRA 3, Dual Beam, Tescan), coupled with energy dispersive X-ray spectrometer (EDX, Oxford Instruments), was used to ascertain the morphologies of the surface of the membrane before and after coupling and quaternization. In order to achieve this, the membrane samples were coated with gold thin film by using sputter deposition. This is to make the samples electrically conductive. The entirety of the sample surfaces was scanned, and images captured at varying magnifications. Comparatively, the varying surface

morphologies of the non-modified, modified only, and modified and quaternized membranes was deduced to analyze the contribution of the modification on the surface morphology.

Cross-section images of the coated membranes were also taken with FESEM to discern between the different layers. To estimate the thickness, a glass slide was cleaned using an identical protocol and dip coated with the silane. The film thickness was then measured using variable angle spectroscopic ellipsometry (VASE). J.A. Woollam Completease software were used for the data analyzing and modeling. By using the ellipsometry the folowing three parameters were determined: film thickness, refractive index (n) and extinction coefficient (k). The ψ and Δ measurement was done at three incident angles 65, 70°, 75° over the spectral range 300-1700 nm (0,73-4.13eV).

By using contact angle measurements with an Attention Theta Optical Tensiometer (Biolin Scientific, Finland), the wettability of the membrane surfaces was analyzed. To obtain accurate results, a small rectangular shape of the samples was cut and fixed on glass slides for a smooth surface. Water droplets of volume ~ 20 μL were carefully placed on the membrane samples and with a high-resolution camera, the image of the samples was captured. An average of 5-6 different measurement locations, were evaluated.

By using a Thermo Nicolet 6700 FTIR spectrometer fitted with Smart Orbit diamond micro-ATR, the surface chemistry of the membrane specimens was analyzed. Prior to the actual samples, background correction was necessary and was duly applied by scanning the empty stage. A total of 32 scans were performed for each measurement and the range of wavenumbers covered was 600 – 4000 cm^{-1}. The resulting spectra for the membrane samples were analyzed for the identification of the functional groups present and relative intensities.

Analysis by using X-ray Photoelectron Spectroscopy (XPS) was used to verify the presence of the coating of silane and its quaternization on the modified membranes. Square-shaped coupons with approximate dimensions 1 cm × 1 cm were cut from the non-coated, coated only and coated & quaternized membranes and mounted on the XPS stage. The analyses were conducted on an Axis Ultra DLD system under ultra-high vacuum conditions (1.6 × 10−12 bar) using a Thermo Scientific ESCALAB 250 Xi x-ray photoelectron spectrometer in the Surface Science Laboratory of the Physics dept., KFUPM. The survey scan was performed in the binding energy range 0–1000 eV with a resolution of 1 eV. High-resolution scans of C 1 s, F 1 s, O 1 s and Si 1s were conducted under similar conditions with 0.05 eV steps, pass energy 20 eV.

1.5 Filtration testing

For this purpose, a custom-made laboratory setup, described in our previous studies[2], was utilized for cross-flow membrane filtration. This consisted of a membrane cell made from stainless steel (CF042SS, Sterlitech, Inc.) with an active area of ~ 42 cm^2. The concentrate was recycled back to the feed tank whereas the permeate was collected in a measuring cylinder as per requirement. A synthetic NaCl solution of approx. concentration 35g/L, representing average seawater TDS, was used as the feedwater. The operating pressure was maintained ~ 800 psi with a high-pressure pump (Wanner Engineering, Inc.) and a flow rate of ~ 5 L/min. The feed temperature was maintained ~ 23ºC by using a constant temperature circulating bath (Polystat, Inc.).

After an initial period of membrane compaction, the setup was run continuously for 2-3 hours and the permeate flux recorded. The percentage of salt rejection was also determined by measuring the TDS of the feed solution and the permeate water collected in a measuring cylinder using an ultrameter (Myron, Inc.). The above procedure was first performed on the non-coated membranes and then repeated for the membranes coated with the silane and also quaternized. For better

comparison, the operational conditions i.e. pump pressure, feed temperature and the flow rate were kept identical. The permeate water flux was calculated by measuring the volume of permeate (mL) collected in a 50 mL measuring cylinder in a given time (10 minutes) and using the equation shown below:

$$J = \frac{V\ (L)}{A\ (m^2)\ x\ T\ (hr.)}$$

Where V is the volume of the permeate water in Liters, A, area of the membrane sheet in meter-square and T, time of the process in hours.

2 Bacterial Adhesion Testing

2.1 Preparation of the bacterial suspension

The anti-adhesion and antibacterial capabilities of the original and modified membranes were investigated with pure cultures of two different types of microorganisms: (i) gram-positive *Bacillus subtilis*, and (ii) gram-negative *Pseudomonas aeruginosa*. The cultures for both were grown in Nutrient Broth (NB) in a shaking incubator (150 rpm) for overnight at 37 °C. The bacterial biomass was washed with PBS after an incubation period in order to remove the media. The final suspensions of both bacterial species were then diluted with sterile 0.9% NaCl to reach concentrations of ≈10^7 colony-forming units (CFU/ml).

2.2 Bacteriostasis Rate Measurement

By standard plate count methods, the antibacterial characteristics of the pristine membrane, coated only and coated & quaternized, were assessed with the purpose of enumerating the number of the viable colonies of bacteria left in the suspensions. The rates of bacteriostasis were adopted to

quantify the bacterial activities for the three different surfaces. The membranes (6 cm^2) were put in 6 well flat-bottom polystyrene plates (Sigma Aldrich) containing $2x10^5$ CFU/ ml of *B. subtilis/P. aeruginosa* suspension for 6 h at 37 °C while shaking at 150 rpm. The membrane samples were removed from the suspension of the bacterial and were diluted using 10-fold serial dilution after incubating them. Thereafter, 100 µl of each diluted bacterial suspension was spread onto agar plates and incubated for 24 h at 37 °C. In the end, the population of the colonies found on the agar plates was enumerated by standard plate count method. The relation below was used to calculate the bacteriostasis rate (B_R):

$$B_R = \frac{A - B}{A} \times 100\%$$

where A denotes population of the colonies on the control plate (without quaternized) and B is the population of colonies on quaternized membranes.

2.3 Bacterial Adhesion Quantification

To perform the adhesion test, 2cm by 3cm ($6cm^2$) of each membrane (without and with quaternization) were immersed into the bacterial suspension in 6 well flat-bottom polystyrene plates. At 150rpm and 37 ^oC for 12 hours, the plates were incubated. After incubation, to remove loosely bound/attached planktonic bacteria, each membrane was removed and washed with DI water. The membranes were then fixed with 2.5% glutaraldehyde solution at 4 °C for 6 h. The membranes were then subjected to a series of dehydration with 30, 50, 70, 90 and 100% ethanol (10 min each) and then dried at 30 °C in a desiccator. Samples were then mounted on aluminum stubs and coated with gold before imaging. In the end, all the samples were studied under a Scanning Electron Microscope (SEM) at an accelerating voltage of 20 kV.

3 Results

3.1 FTIR spectra

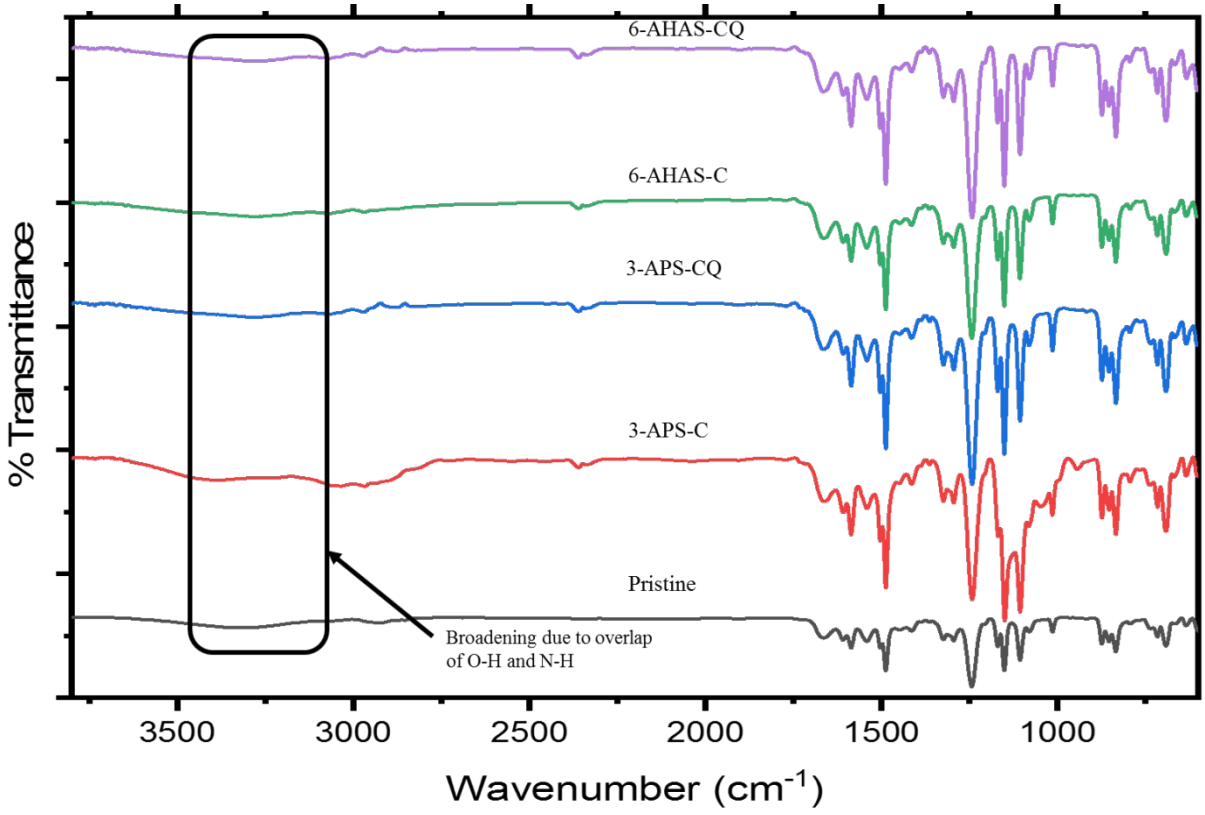


Figure S3 Complete FTIR spectra for the original and modified membranes. Note the broadening of O-H peak ~ 3300 due to overlap with the N-H. Also, note the relatively higher peak intensities in the range 1,000 – 1,500 for the coated membranes.

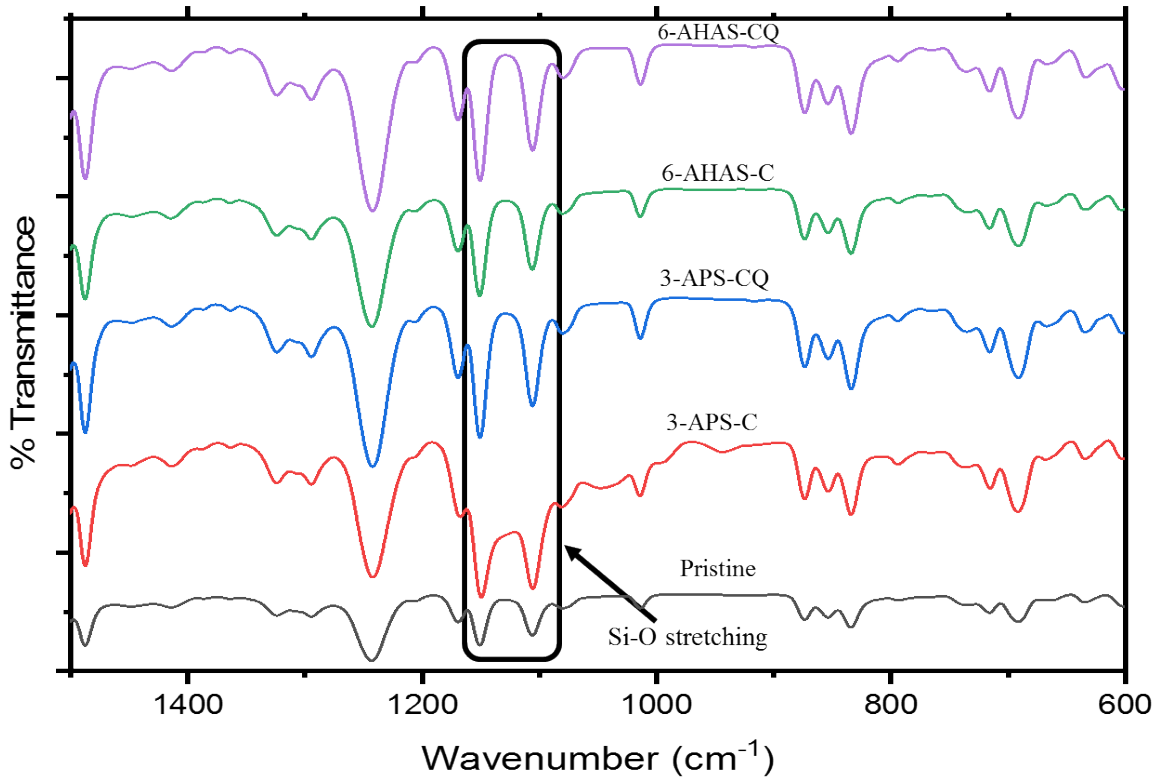
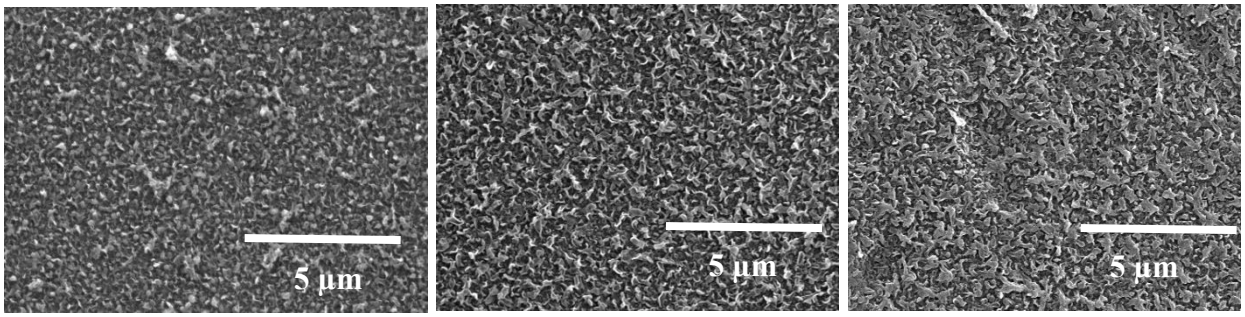
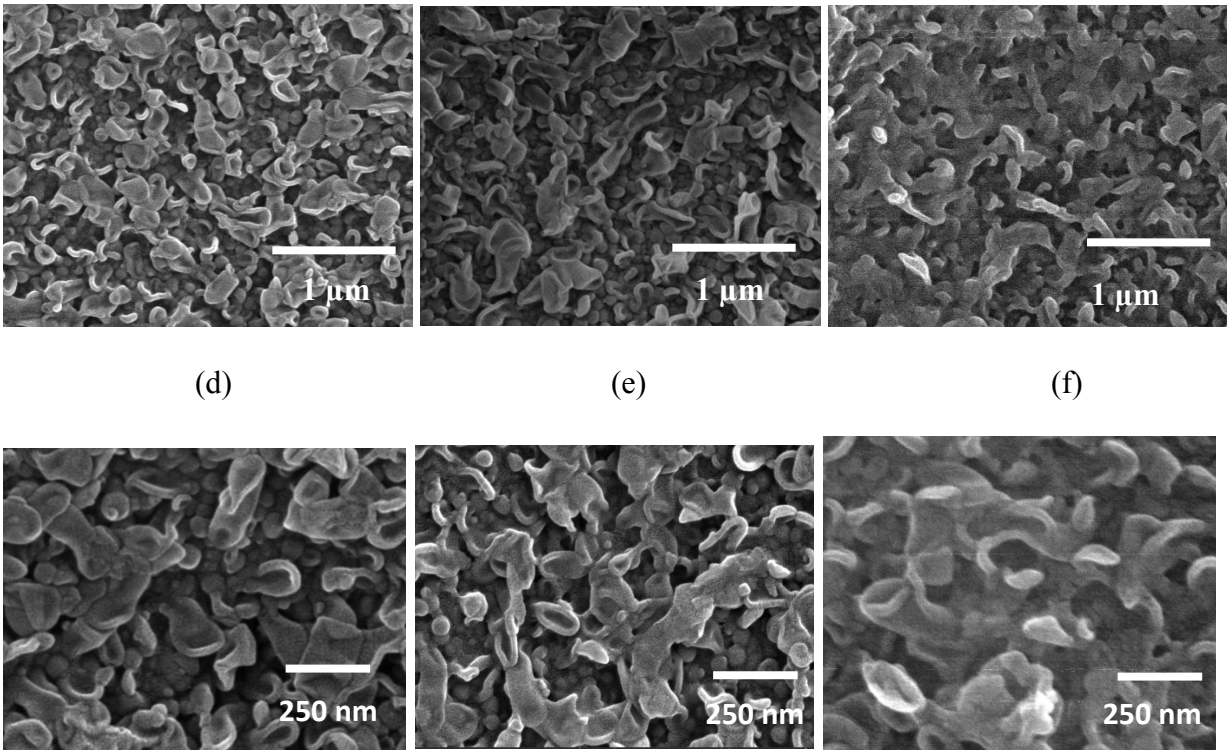


Figure S4 Enlarged view of the FTIR spectra in the footprint region. The encircled area contains the peaks around 1100 and 1150 corresponding to Si-N and Si-O respectively. Note the presence of peaks at almost identical wavenumbers for the uncoated membrane albeit with much lower intensity. The deposition of silane film and its subsequent quaternization results in increased intensity and peak sharpening.

3.2 Surface Morphology



(a) (b) (c)

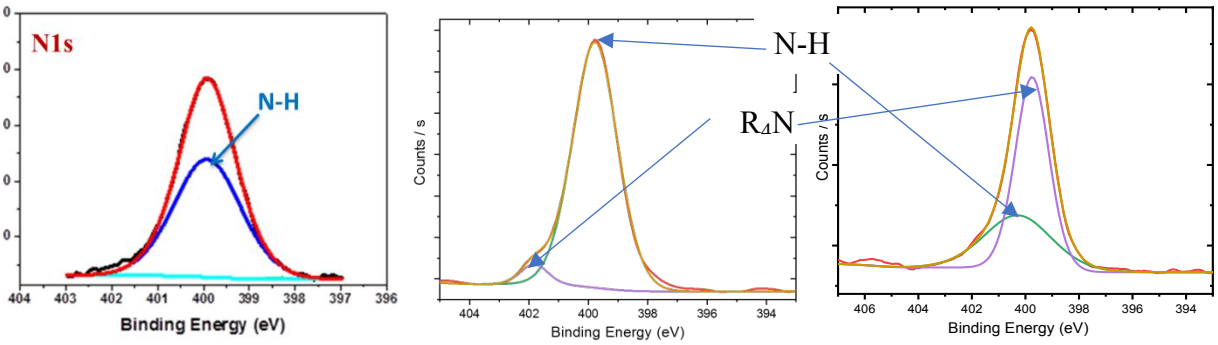


(d) (e) (f)

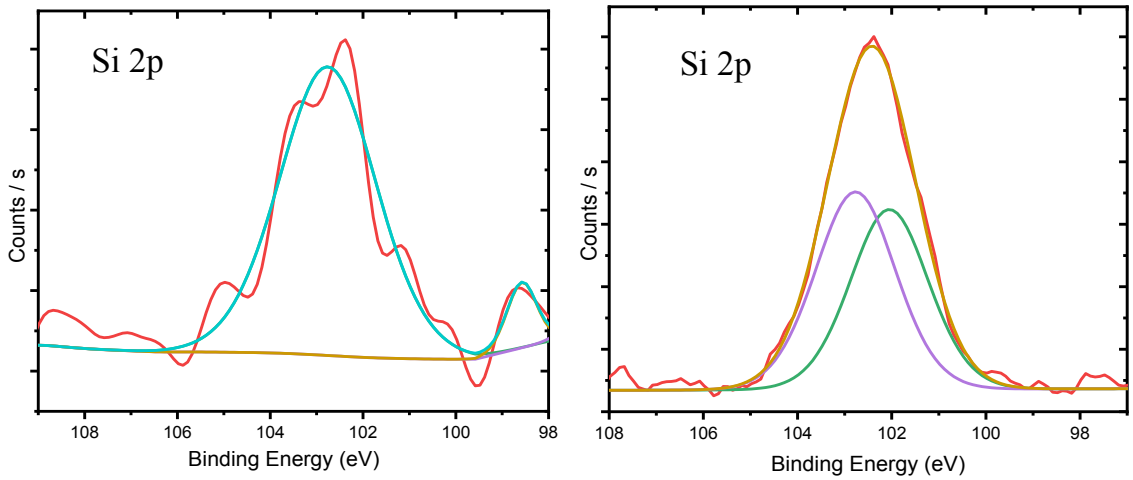
(g) (h) (i)

Figure S5 FESEM images of the membrane before and after modification with silane at different magnifications. (a, d, g) uncoated (b, e, h) coated with 6-AHAS, and (c, f, i) coated with 6-AHAS and quaternized. Note the leaf-like morphology and the ridge and valley structure associated with the polyamide layer of the RO membrane. Also note filling of valleys esp. after the quaternization that is more prominent in the higher magnification image

3.3 Surface Elemental Analysis



(a) (b) (c)



(d) (e)

Figure S6 High resolution XPS scans for the coated and non-coated membranes: N 1s for the (a) original membrane (b) after silane coating (c) coated and quaternized Similarly, Si 2p spectra for the membranes coated with 6-AHAS (d) coating only (e) coated and quaternized. Note the difference in the peaks for these two elements before and after quaternization. Before quaternization the peak corresponding to the amide bond (N-H) dominates, whereas quaternization results in a significant increase in the intensity of the quaternary ammonium (R_4N^+). For Si 2p, a lone peak corresponding to Si-O (~ 103 eV) is visible after the coating, and two distinct convoluted peaks attributed to the former and Si-N can be observed.

References

[1] N. Kim, D. H. Shin, and Y. T. Lee, Effect of silane coupling agents on the performnace of RO membranes, *J. Membr. Sci.* 300 (2007) 224-231

[2] A. Matin, H. Shafi, M.Wang, Z. Khan, K. Gleason, F. Rahman, Reverse osmosis membranes surface-modified using an initiated chemical vapor deposition technique show resistance to alginate fouling under cross-flow conditions: Filtration & subsequent characterization, *Desalination* 379 (2016) 108–117