Environmental Science
Water Research & Technology

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Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-10-2018-000690.R1
Article Type:	Paper
Date Submitted by the Author:	30-Nov-2018
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Water Impact Statement

Municipal wastewater contains a high concentration of nitrogen in the form of ammonium, which pollutes the environment if not properly removed before discharging. However, the engineering processes for nitrogen removal are energy intensitive. Recovery of ammonium from domestic wastewaters can covert the waste into resources. This study reports concentrating ammonium in the wastewater using a surface modified nanofiltration membrane operating in forward osmosis mode. Ammonium rejection by the modified membranes was greater than 99% for the synthetic ammonium solution.

Concentrating ammonium in wastewater by forward osmosis using surface modified nanofiltration membrane

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Keywords: Surface modification, Nanofiltration, Ammonium, Forward osmosis

Abstract

Municipal wastewater contains a high concentration of nitrogen in the form of ammonium, which pollutes the environment if not properly removed before discharge. However, the energy intensive processes necessary to convert the biologically available forms of nitrogen into the unfixed elemental form (N_2) during wastewater treatment contradict the costly industrial efforts to achieve the opposite (i.e. Haber process) for production of nitrogen fertilizers for agricultural uses. Recovery of ammonium from domestic wastewater should be a priority for wastewater treatment plants to covert the waste into resources. This study reports developing a surface modified nanofiltration membrane operating in forward osmosis mode for concentrating ammonium in wastewater. Surface modification was accomplished using dicyclohexylcarbodiimide (DCC) as a cross-linking agent to graft polyethylenimine (PEI) on the polyamide (PA) thin film composite (TFC) membrane. Changes in membrane surface chemical structure and zeta potential demonstrated the successful incorporation of PEI. The modified membranes had similar surface roughness to the virgin membrane but improved hydrophilicity. Filtration tests using synthetic ammonium solutions demonstrated improved water flux and reduced reverse solutes (Mg^{2+} and Cl^- ions) flux in some of the modified membranes. All PEI grafted membranes had improved ammonium rejection for synthetic ammonium solutions as well as a secondary return activated sludge sample from a wastewater treatment plant. Ammonium rejection by the modified membranes was greater than 99% for the synthetic ammonium solution. The rejection rate declined to 89.3% for treating real wastewater but was much improved in comparison to 75.5% rejection by the virgin membrane. PEI-modified membranes present a potential technology for the collection and reuse of ammonium from wastewater sources.

1. Introduction

Domestic and industrial wastewaters contain large amounts of nitrogenous compounds, including ammonia.[1-6] In fact, up to 40-50% of the total nitrogen in a municipal wastewater treatment plant is in the form of ammonium ion (NH_4^+).[7] Discharge of these nitrogenous compounds into the environment can cause eutrophication of the surface waters[8] and toxic effects on aquatic life even in very low concentrations.[9] To protect aquatic ecosystems and human health, the U.S. Environmental Protection Agency (EPA) mandates nitrogen removal before wastewater can be discharged to the environment.[10]

Biological treatments that include aerobic nitrification and anaerobic denitrification processes[11] are the most commonly used approaches to treat wastewater for ammonium removal in wastewater treatment plants (WWTPs). Both processes are costly in terms of energy, maintenance, and operation during wastewater treatment. For example, nitrification requires over four times more oxygen than is needed for organic carbon removal in wastewater.[12] Recently, a novel process was discovered in which ammonium is converted to dinitrogen gas under anoxic conditions with nitrite as the electron acceptor. This process, named Anammox (anaerobic ammonium oxidation), reduces the energy intensity of treatment by short-circuits the nitrification step.[13, 14] However, the need to convert the biologically available forms of nitrogen into nitrogen gas remains, which contradicts costly industrial efforts for production of nitrogen fertilizers for agricultural uses.

Therefore, recover the ammonium from domestic wastewater should be a priority for wastewater treatment plants to covert the waste into resources. So far, there are no cost-effective methods available to achieve this. Most existing methods that can be used to recover ammonium, such as air stripping, electrodialysis, struvite precipitation and membrane technologies like

reverse osmosis (RO), require the ammonium concentration about 20 times higher than that in domestic wastewater (40–60 mg/L of NH_4–N). Therefore, none of the current methods are economical for ammonium recovery. Here, we propose using a forward osmosis (FO) process to concentrate the ammonium in the wastewater for down stream recovery.

FO follows the natural osmosis gradient for solvent diffusion through membrane from feed solution (FS) with higher water chemical potential to draw solution (DS) with lower water chemical potential.[15-19] FO has been proposed for treating complex water matrices due to its low fouling propensity and low energy requirements.[20, 21] However, past research has found relatively low rejection of ammonium (48.1±10.5% rejection) in a pilot-scale FO system, despite its high efficiency in separation of organic matter and phosphorus.[21] This is largely due to the small molecular weight of ammonium ions, similar to that of water molecules, which are permitted by diffusion through the membrane. To increase ammonium rejection by FO, membrane properties have to be improved.

Considerable efforts have been made in exploring appropriate FO membranes on ready-made membranes. Chemical modification has become an important method in novel FO membrane exploration in recent years.[18, 22] One strategy for improving ammonium rejection is to create a positively charged, highly hydrophilic membrane surface that repeals the positively charged ammonium ions, while maintaining a greater affinity for the diffusion of water molecules through membrane. Membrane surface modification has been widely used to improve membrane properties for various purposes.[23-27] Many efforts have been made to develop new membranes with positively charged surfaces.[18, 28-32] Among many physical- and chemical-based surface treatment methods, polyethylenimine (PEI) has shown promise as the aqueous reactant with polyamine (PA), which forms amine-rich polyaminde layer on thin film composite (TFC)

membrane surfaces through interfacial polymerization.[28, 33] Another approach is the use of carbodiimide-induced grafting with PEI to dramatically improve the hydrophilicty of the membrane surface, which not only provides a positively charged surface to repel positively charged ions, but also has excellent antifouling properties due to the membrane hydrophilicity.[33, 34]

Here, we report surface modification of PA TFC membranes with nanofiltration (NF) properties. Compared to the typical RO-like FO membranes that are used for brackish water or seawater desalination applications, the NF-like FO membranes have great potential for organic wastewater treatment due to their higher water flux.[35, 36] Abdullah et al. (2018)[37] demonstrated high water flux and minimum reverse solute flux using TFC NF membrane (NF90 and NF270, Dow FilmTech) in FO mode in treating palm oil mill effluent with divalent salts as the draw solution. In this study, $MgCl_2$ was used as the draw solution to evaluate ammonium rejection of the modified TFC NF membrane in FO mode in synthetic ammonium solution and in return activated sludge (RAS) from a wastewater treatment plant. The separation performance of the modified membranes was investigated with regards to permeability, selectivity toward ammonium ions, as well as the surface physicochemical properties.

2. Materials and Methods

2.1. Membrane modification

A PA TFC NF membrane (NFS, molecular weight cutoff of 100-250 Da) from Snyder Filtration, Inc. was used as the virgin membrane for surface modification. The membrane has approximate molecular weight cutoff of 100-250Da, minimal $MgSO_4$ rejection of 99.5% and average NaCl rejection of 50-55% under 760 kPa operation pressure (Snyder Filtration

http://synderfiltration.com/nanofiltration/nfs-membrane/). Branched PEI solution with a molecular weight (MW) of 70,000 (30 w/v% solution in water), N,N′-dicyclohexylcarbodiimide (DCC), dimethylsulfoxide (DMSO), ammonium chloride, and magnesium chloride were purchased from Fisher Scientific Inc. and were used without further purification. The proposed mechanism for the membrane surface modification is shown in Figure 1. DCC is used to react with carboxyl groups on the membrane surface to form a reactive o-acylisourea intermediate, which is then displaced by nucleophilic attack from primary amino groups of PEI in the reaction medium. The primary amine forms an amide bond with the carboxyl group, and an insoluble dicyclohexyl urea (DCU) by-product is generated that can be separated.

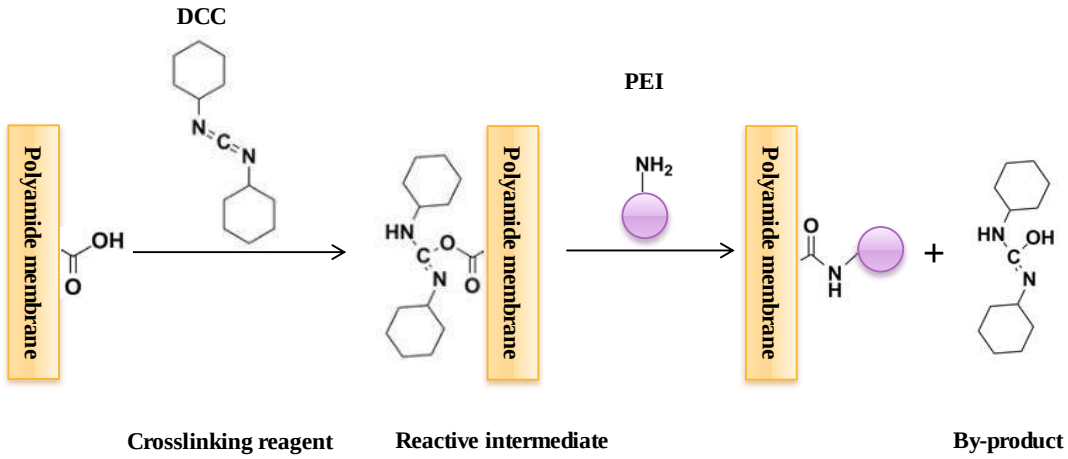


Figure 1. Schematic of the membrane surface modification mechanism and process

In preparation for membrane surface modification, DCC (2.9 mmol) was dissolved in DMSO (10 part DMSO and 1 part DI water) as the activation solution. PEI was then added to the activation solution in various concentrations to form the final grafting solution. Six concentrations of PEI, 0.2, 0.6, 1, 1.5, 3, or 4.5% (w/v), was tested for PEI incorporation to PA. Since the NFS membrane's polyester support and microporous polysulfone interlayer are sensitive to DMSO, the membrane piece was fixed in a 6 cm × 18 cm plate-frame cassette to

ensure the reactant solutions only had contact with the PA active layer. A 60 mL grafting solution was poured onto the membrane surface for reaction at room temperature (22°C) for 15 hours. At the end of incubation, membranes were washed several times with DI water to remove any unreacted chemicals and finally stored in DI water at 4°C until use. No penetration of DMSO to the support layer or damage of the support layer was observed during the reaction period. The modified membranes were named based on the concentration of PEI in the grafting reaction, for example, reaction with 0.2% PEI is denoted as 0.2% PEI-NFS. The unmodified Synder's NFS membrane was denoted as the virgin NFS.

It is important to mention that before adoption of NFS membrane for surface modification, we compared NFS membrane and DOW SW30XLE RO membrane (Dow Filmtec^{TM}, Midland, MI) for operation in the FO mode. This preliminary study showed that under the same osmotic gradient, NFS has averaging 2.7 times greater water flux than SW30XLE in the FO operation (data not shown). This result agrees with previous work demonstrating the NF-like FO membrane to produce higher water flux.[36, 37] A HTI FO membrane (HTI-ES, Albany, USA) was also initially used for comparison but was terminated due to discontinuing of the product by the manufacturer and the poor ammonia rejection.[20] NFS was used as the sole membrane for surface modification to demonstrate that surface electrostatic repulsion plays a major role of ammonium ion rejection instead of the membrane pore size.

2.2. Membrane surface characterization

2.2.1. Raman spectroscopy measurement

The membrane surface chemical structure and composition of NFS membrane before and after modification were determined by a Rennishaw InVia Raman microscope in the region of 200–3,600 cm^{-1} to confirm the grafting of PEI onto the membrane surface. The Raman spectra of the

virgin NFS membrane and the PEI (liquid solution) were also acquired to identify the PEI signal peaks on the modified NFS membrane surfaces. The analysis for PEI solution was performed at room temperature with a 532 nm laser as the radiation source under a 10% power of the nominal laser intensity and an integration time of 10 s; whereas the analysis for virgin and modified NFS membranes was conducted with a 785 nm laser. The baseline was corrected for all spectrums using WIRE 3.4 software (Reinshaw). The maximum amount of PEI grafted onto the membrane surfaces was determined based on significant differences in the expected PEI signal peak counts.

2.2.2. Surface roughness, charge and hydrophilicity measurements

The morphology and surface roughness analyses were carried out by 3D Laser Scanning Confocal Microscope (VK-X250, KEYENCE Corporation, USA) at room temperature with scanning area of 10 × 10 μm^2. All the reported surface roughness values are an average obtained from three different positions on each membrane.

A SurPASS streaming potential analyzer (Anton Paar, Graz, Austria) with an adjustable gap cell was used to measure electrokinetic properties of membrane surface. Membranes were cut and immobilized on the sample supports (20 mm × 10 mm) within the cell, and the gap was adjusted to approximately 100 μm. The zeta potential (ζ) of each membrane was calculated from the streaming potential using the Fairbrother-Mastin approach as follows:

$$\zeta = \frac{dU}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{1}{R} \times k_{high} \times R_{high} \quad (1)$$

where, $\frac{dU}{dp}$ is the streaming potential coefficient, η is the viscosity of the electrolyte solution, $\varepsilon \times \varepsilon_0$ is the dielectric coefficient of the electrolyte solution, R is the electrical resistance inside the streaming channel, k_{high} is the electrolyte conductivity and R_{high} is the resistance inside the

streaming channel at high ionic strength.[38] The zeta potential was measured in 1 mM KCl at room temperature over a pH range of 3 - 9 through titration with 0.5 N NaOH.

The hydrophilicity of membrane surfaces was tested using a Goniometer (OPTIXCAM SUMMIT K2, Rame-Hart, Inc., USA) equipped with a video camera. DI water (1 μL) was placed in six random locations on each membrane sample at room temperature and an image was acquired of the water droplet. The left and right contact angles were measured using Toup View Image software. For each sample, six measurements were averaged to get a reliable value.

2.3. Membrane filtration properties

2.3.1. FO operational conditions

A cross flow FO cell (Sterlitech CF042D-FO Cell, USA) was used to test the FO filtration properties in batch mode (Figure 2). The FO cell had an effective membrane area of 42 cm^2. In FO application mode, the active membrane surface was in contact with the feed solution (FS) and the support layer (back layer) was in contact with draw solution (DS). Both solutions (0.25 L for DS and 0.5 L for FS) were pumped in the counter-current direction by peristaltic pumps at flow rate of 60 mL/min at room temperature unless indicated otherwise. The flow rate is within the laminar region of the Reynolds number to balance the need for pumping energy conservation and stable permeate flux.[17] For ammonium rejection experiments, 50 ppm NH_4^+ in the form of NH_4Cl in DI was used as FS. In all experiments, 1 M magnesium chloride ($MgCl_2$) aqueous solution was used as DS at the beginning of the batch study. Each experiment ran for 28 h, during which time water flux was determined using a digital balance for changes in water volume in the FS and DS tanks. The slow progressive dilution of DS by permeate flux occurred over the experimental period but did not significantly influence the comparison of properties between modified and un-modified membranes.

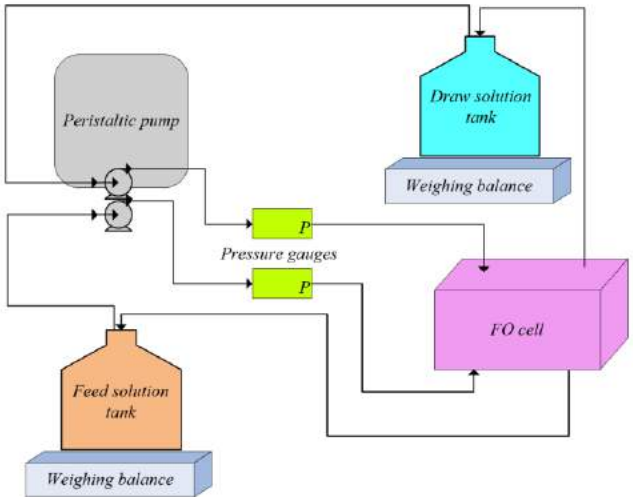


Figure 2. Schematic of the laboratory-scale forward osmosis (FO) system set up.

The reverse solutes (Mg^{2+} and Cl^-) flux from DS to FS was determined by the initial and final volume of FS and the ion concentrations measured by ion chromatography (IC, 940 Professional IC Vario, Metrohm, USA). For ammonium rejection, ammonium concentrations of initial FS before the FO process and final DS after the FO process were measured using IC. In addition, the AmVer™ Salicylate Test 'N Tube™ method was also applied for low range (0-2.50 mg/L NH_3-N, Hach method 10023) and high range (Hach method 10031, 0-50 mg/L NH_3-N) ammonia nitrogen using a DR/890 portable colorimeter to calculate the ammonium rejection.

In addition to using 50 ppm NH_4^+ synthetic solution as FS, a return activated sludge (RAS) from the secondary clarifier of a local wastewater treatment plant was used as FS to evaluate the membrane application to a real environmental sample. The water fluxes, reverse solutes (Mg^{2+} and Cl^- ions) fluxes, and ammonium rejection by the virgin NFS membrane and the 1.5% PEI-NFS membrane were compared using 1 M $MgCl_2$ solution as DS and a cross flow rate of 60 mL/min at 25 °C.

2.3.2. Filtration property calculations

The water flux across the FO membrane was calculated using the following equation[39-41]:

$$J_w = \frac{\Delta V}{A_m . \Delta t} = \frac{\Delta m}{\rho . A_m . \Delta t} \quad (2)$$

where, J_w is the water flux (L/m^2.h or LMH), ΔV (L) is the volume change of DS over time interval Δt (h), A_m (m^2) is the effective membrane area, ρ is the density of the DS (g/L), and Δm (g) is the weight change of the DS. The reverse solutes flux takes place from DS in the reverse direction of the water flux and is calculated with the following equation[39]:

$$J_s = \frac{C_t V_t - C_0 V_0}{A_m . \Delta t} \quad (3)$$

where, J_s is the reverse solute flux (g/m^2.h or *gMH*), C_0 (g/L) and V_0 (L) are the initial concentration of solutes and initial volume of the FS, respectively. C_t (g/L) and V_t (L) are the solutes concentration and the volume of the FS measured at time of t, respectively.

The ammonium rejection percent (R%) by the membrane was calculated using the following equation[20, 32]:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where, C_p and C_f are the ammonium concentration permeated through membrane from FS to DS and initial ammonium concentration in FS before FO process, respectively.

3. Results and discussion

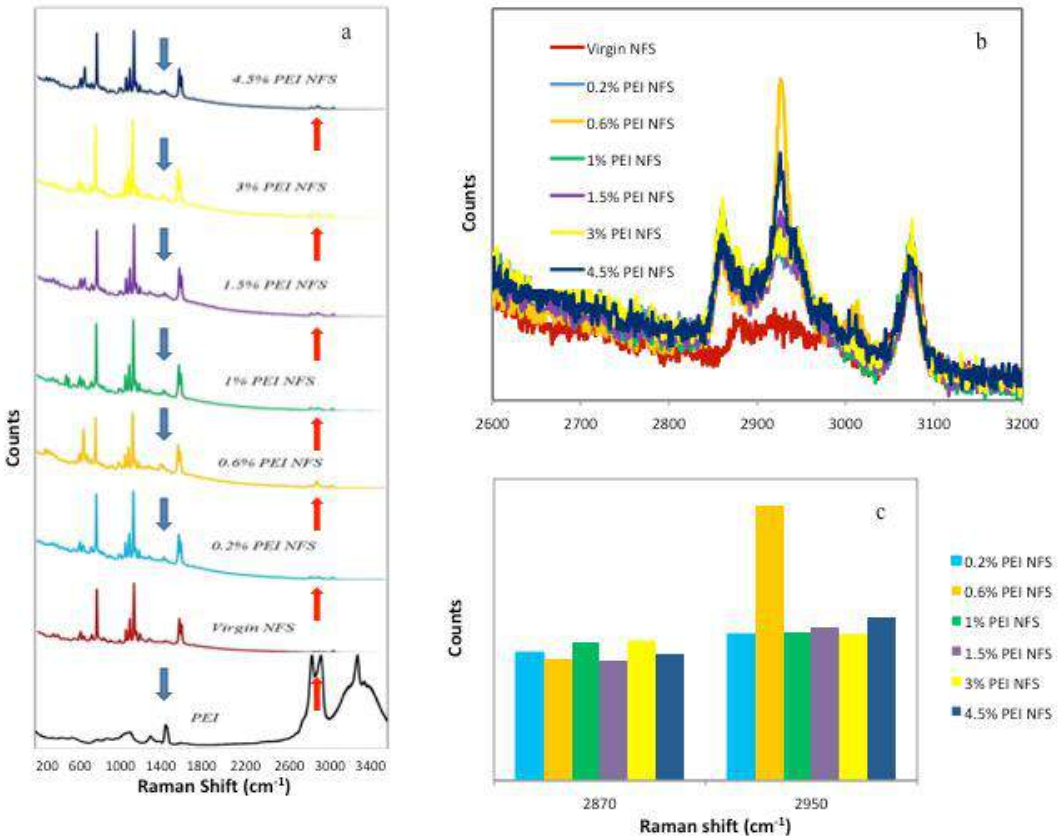
3.1. Characterization of membranes

3.1.1. Raman spectroscopy analysis

Changes of chemical groups on surface modified NFS membranes compared to the virgin NFS membrane are shown in Figure 3. Raman spectra of PEI solution have characteristic peaks at 1460, 2873, 2956, and 3309 cm^{-1}. The bands at 1460 and 3309 cm^{-1} correspond to CH_2

deformation vibration and N-H vibration, respectively; whereas the bands at 2873 and 2956 cm^{-1} are assigned to the C-H vibration.[42] Raman spectra of the virgin NFS membrane has major spectral peaks located at Raman shifts of 792, 1076, 1111, 1150, 1589, and 1611 cm^{-1}, which are likely associated with the polyamide functional groups.[43] Specifically, the bands at 792, 1589, and 1611 cm^{-1} are associated with the asymmetric C-N-C stretch of tertiary amides, aromatic in-plane ring bending vibration, and aromatic amide groups, respectively; whereas, the bands at 1076, 1111, and 1150 cm^{-1} are assigned to the C-N stretching vibrations of both the piperazine rings and the amide groups.[39]

Compared with the virgin NFS membrane, all the PEI modified NFS membranes have peaks formation at approximately1460, 2870 and 2950 cm^{-1} (Figure 3a, b), which are consistent with peaks belonging to PEI in its natural state (liquid solution). This result indicates that PEI was successfully grafted onto the NFS membrane. In addition, as shown in Figure 3c, the counts or intensity of 2873 and 2956 cm^{-1} peaks change with the variation of PEI concentration in grafting solution. The amount of PEI grafted onto the membrane surface is determined by Raman spectroscopy based on the PEI signal peak counts (Figure 3c). It seems that the PEI concentrations as low as 0.6% (w/v) are suitable for grafting solutions.



249

250 Figure 3. Raman spectra of PEI solution, virgin NFS membrane, and PEI grafted NFS

251 membranes (a), and an overlay image that compares Raman shift of 2,600 - 3,200 cm^{-1} (b). The

252 PEI signal peak area on membrane surface is quantified in (c). Arrows on (a) indicate the new

253 peaks identified on membrane surface that correspond to PEI peaks.

254

255 **3.1.2. Membranes surface roughness**

256 Five surface roughness measurements, including arithmetic mean height (Sa), maximum height

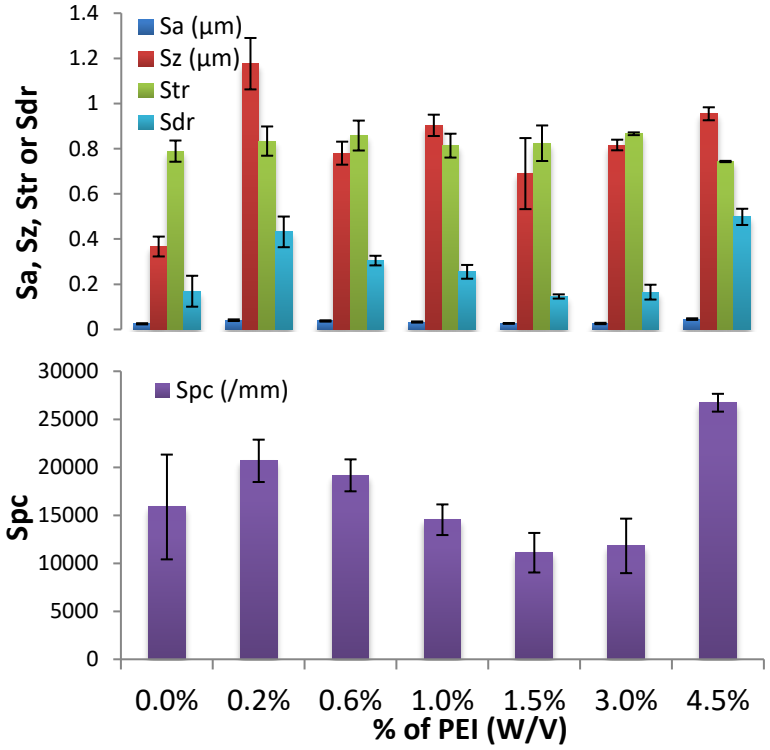
257 of the surface (Sz), texture aspect ratio (Str), arithmetic mean peak curvature (Spc), and

258 developed interfacial area ratio (Sdr), were used to compare the virgin NFS membrane and PEI

259 grafted NFS membranes (Figure 4). The results confirm that both the virgin NFS membrane and

260 PEI grafted NFS membranes have relatively uniform surfaces. Sz values are slightly higher by

261 PEI grafting on the surface of PA membrane. Sdr and Spc are also greater for 4.5% PEI-NFS
262 membrane ($p<0.05$) but are not significantly different for other PEI grafted NFS membranes in
263 comparison with the virgin membrane ($p>0.05$). This result suggests 4.5% PEI-NFS membrane
264 likely become rougher than the virgin membrane. But there is no significant difference in other
265 roughness measurements of the modified membranes when compared with the unmodified
266 membrane.



267

268 Figure 4. The surface roughness measurement (arithmetic mean height (Sa), maximum height of
269 the surface (Sz), texture aspect ratio (Str), arithmetic mean peak curvature (Spc), and developed
270 interfacial area ratio (Sdr) of the virgin NFS membrane and PEI grafted NFS membranes.

271

272 **3.1.3. Membranes surface charge**

273 The zeta potential measurements of the virgin NFS membrane and PEI grafted NFS membranes
274 as a function of pH are shown in Figure 5. The isoelectric point (IEP) for each membrane is

indicated by the horizontal line crossing zero zeta potential. The virgin NFS membrane has an IEP of 3.75. After the PEI grafting, the IEP for the PEI grafted NFS membranes are shifted to higher values due to increases in positively charged amine groups attached to the surface. These positive charge groups can be useful for improving ammonium rejection under a range of environmental conditions. The changes in surface charge on the membrane is best explained by amine protonation at pH values below the IEP, while increasing pH beyond the IEP results in deprotonation of carboxyl groups and a negative surface charge as shown by previous literatures.[33, 35, 44]

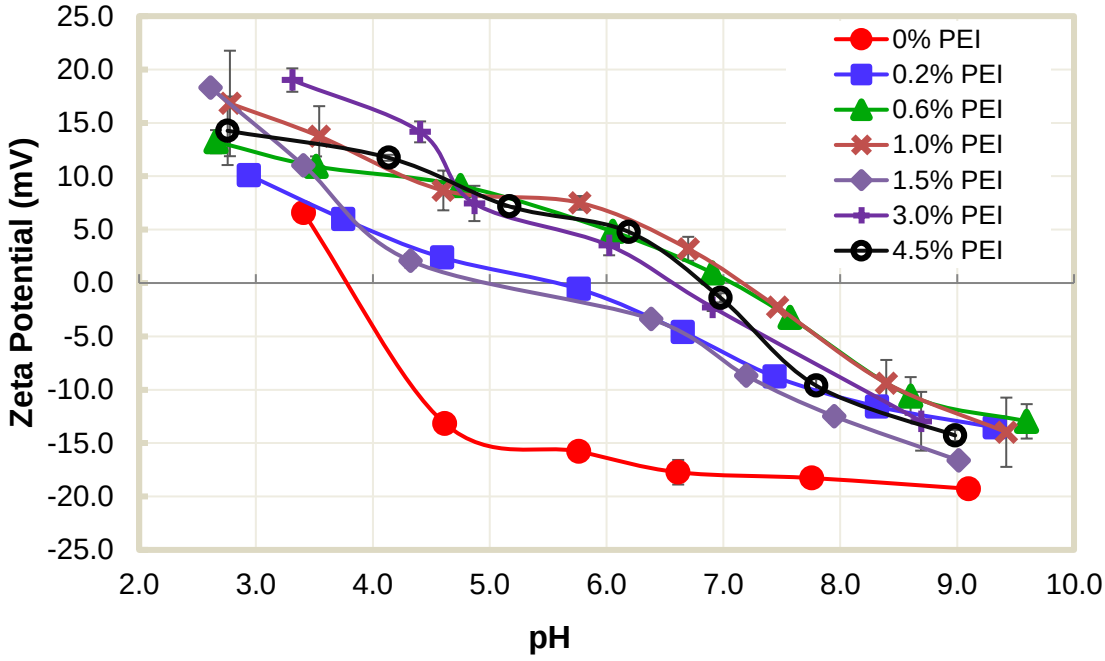


Figure 5. Zeta potential of the virgin NFS membrane and PEI grafted NFS membranes as a function of pH.

In all pH ranges, the zeta potential values of the PEI grafted NFS membranes are higher than that of the virgin NFS membrane. This indicates that the PEI grafted NFS membranes have more positively charged molecules in comparison with the virgin membrane. At pH value <5.5,

all modified membranes displayed net positive charge on surface. At the pH>5.5, the additional amine groups on membrane surface may translate into higher electrostatic repulsion of ammonium in comparison with the virgin NFS membrane.

3.1.4. Membranes water contact angle

The hydrophilicity of the membrane can affect its flux and antifouling ability.[32, 33] Comparisons of membrane surface hydrophilicity using water contact angle of the virgin and modified NFS membranes (Figure 6) indicate that water contact angle of the virgin NFS membrane is 49.79°, which is greater than all the PEI grafted NFS membranes. An average value for all PEI grafted member is 45.25°, in which 0.6% PEI-NFS membrane has the lowest contact angel of 43.51° and 4.5% PE-NFS membrane has the contact angle of 48.71°. Lower water contact angles illustrate that more water molecules can penetrate into the membrane surface and thus greater hydrophilicity of the membrane surface. Both the chemical composition and the surface geometrical structure govern the wettability of a solid surface.[33, 45] Therefore, the introduction of exposed polar groups (amine groups) on the membrane surface likely improved surface hydrophilicity after the PEI grafting.[33] These results are in agreement with the Raman spectroscopy data and zeta potential results, confirming the grafting of PEI on the PA NFS membrane surface. On the other hand, the higher water contact angel observed on 4.5% PEI-NFS membrane may be explained by the increased roughness of the membrane surface as shown by the surface roughness measurements in spite of the addition of polar groups on membrane surface.

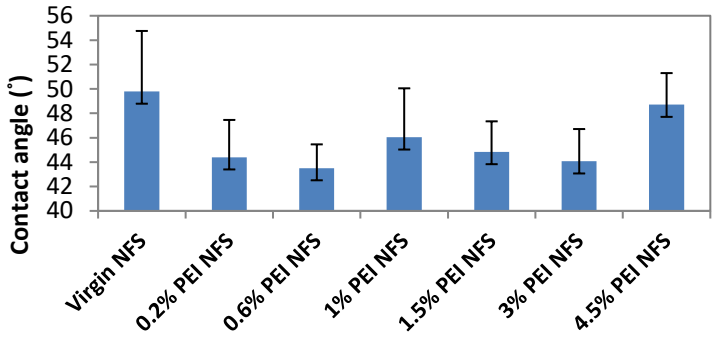
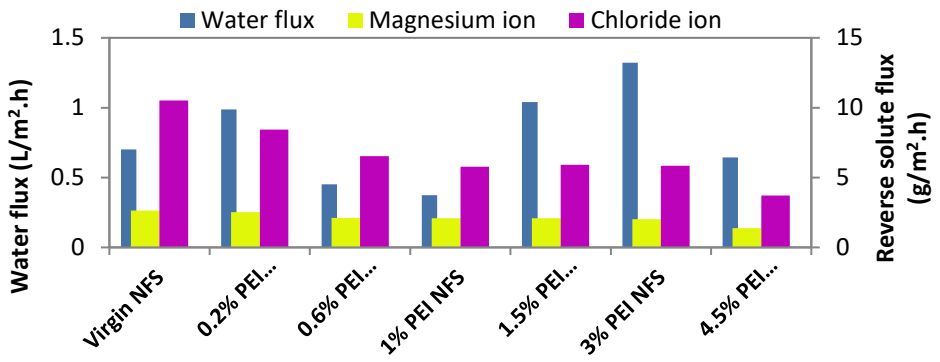


Figure 6. Water contact angle of the virgin NFS membrane and PEI grafted NFS membranes

3.2. Membranes filtration performance

The ideal FO membrane should have no reverse solute flux and a high water flux. Reverse solute flux can cause internal concentration polarization (ICP) and membrane fouling.[39, 46] Solute flux also decreases the osmotic pressure difference across FO membranes.[18] Comparisons of the membrane filtration performance for the water fluxes and reverse solutes (Mg^{2+} and Cl^- ions) fluxes of the virgin NFS membrane and the PEI grafted NFS membranes are shown in Figure 7. The water flux of the virgin NFS membrane was ~0.70 L/m^2.h at the cross flow rate of 60 mL/min. Three of six PEI modified membrane showed improved water fluxes but overall the water fluxes of the PEI modified NFS membranes ranged between 0.37 and 1.32 L/m^2.h. The variation of water flux may be caused by two conflicting factors associated with PEI grafting. First, the improvement of membrane surface hydrophilicity by PEI incorporation can facilitate water molecules' penetration into membranes that leads to the increase of membrane water flux. Second, the addition of PEI on PA can block membrane pores and increase trans-membrane resistance of water molecules, which results in a reduction of water flux. Thus, the final variation of water flux can depend on which of these two factors dominates.[32, 33, 47]



329

330 Figure 7. Water fluxes and reverse solutes (Mg^{2+} and Cl^- ions) fluxes of the virgin NFS
331 membrane and the PEI grafted NFS membranes.

332

333 The best water flux is found in 3% PEI-NFS membrane, which has the improved surface
334 smoothness (Figure 4), increased positive charges (Figure 5) and enhanced hydrophilicity
335 (Figure 6). The 1.5% PEI grafted membrane has the second best water flux, smoothness and
336 hyrophilicity. Therefore, 1.5% to 3% of PEI may be the ideal condition for membrane surface
337 modification. It was also noted that the water flux rate observed in this study is slightly lower
338 than a previous study reported by Cornelissen et al.[48] using a similar type of membrane.
339 However, that study was carried out in a much faster cross flow rate (nearly 100 times higher)
340 and using a higher concentration of drawn solution.

341 As shown in Figure 7, the reverse solutes (Mg^{2+} and Cl^- ions) fluxes of the virgin NFS
342 membrane are higher than those of the PEI grafted NFS membranes. This result suggests the
343 PEI-NFS membranes have improved properties for reducing reverse solute flux. In addition, the
344 reverse solutes (Mg^{2+} and Cl^- ions) fluxes were reduced in general with increasing PEI
345 concentration from 0.2% to 4.5% (Figure 7). Lower reverse solute fluxes can avoid the osmotic
346 pressure decrease caused by reverse solute diffusion and decline in water flux.[18] Furthermore, the
347 nanopore size plays a key role in reverse solute flux. The Cl^- ion reverse diffusion from DS to FS

348 is approximately three times higher than that of Mg^{2+} ion due to different membrane selectivity
349 to monovalent vs. divalent ions (Figure 7).

350 The ratio of water flux, J_w, to reverse solutes (Mg^{2+} and Cl^- ions) flux, J_s, in the FO
351 process (called the reverse solute flux selectivity) is commonly used to quantify the FO
352 performances.[49] Table 1 compares the reverse solutes (Mg^{2+} and Cl^- ions) flux selectivity of the
353 virgin NFS membrane and the PEI grafted NFS membranes at experimental conditions of 1 M
354 $MgCl_2$ solution as DS, flow rate of 60 mL/min, and room temperature (25 °C). These results
355 confirm that the PEI grafted NFS membranes have improved reverse flux selectivity in
356 comparison with virgin membrane in most cases.

357 Table 1. Comparison of the reverse solutes (Mg^{2+} and Cl^- ions) flux selectivity of the virgin NFS
358 membrane and the PEI grafted NFS membranes

Membrane sample	The reverse solute (Mg^{2+} ion) flux selectivity (L/g)	The reverse solutes (Cl^- ion) flux selectivity (L/g)
Virgin NFS	0.266	0.0667
0.2% PEI NFS	0.392	0.1173
0.6% PEI NFS	0.214	0.0691
1% PEI NFS	0.179	0.0648
1.5% PEI NFS	0.498	0.1758
3% PEI NFS	0.658	0.2257
4.5% PEI NFS	0.464	0.1726

359

360 When comparing ammonium rejection of PEI grafted membranes with virgin NFS
361 membrane using pure NH_4Cl solution, the results showed that the virgin NFS membrane has
362 relatively high ammonium rejection rate (~97%) when operating in the FO mode in comparison
363 with previous reports of ammonium rejection in FO operation using TFC embedded polyester
364 screen supported HTI-ES membrane (35.8%).[20] Grafting of PEI on NFS membrane further
365 improved the ammonium rejection by additional 2-3% for the synthetic ammonium solution
366 without exception.

To test the applicability of PEI-NFS membranes for concentrating ammonium in real wastewater, 1.5% PEI-NFS membrane was compared with virgin NFS membrane using RAS from secondary clarifier of a local wastewater treatment plant. The measured characteristics of RAS are given in Table 2. Ammonium rejections by the virgin NFS membrane was decreased to 75.5% for treating the RAS but the PEI-NFS faired better with an average of 89.3% ammonium rejection. This increase in ammonium rejection may be explained by repulsion due to the increased positively charged molecules on membrane surface from the PEI grafting. The reverse solute fluxes of 1.5% PEI NFS membrane (2.43 $g/m^2.h$ for Mg^{2+} ions and 10.04 $g/m^2.h$ for Cl^- ions) were also much lower than those of the virgin NFS membrane (3.19 $g/m^2.h$ for Mg^{2+} ions and 15.72 $g/m^2.h$ for Cl^- ions). However, water flux of the virgin NFS membrane (0.58 $L/m^2.h$) was slightly higher than that of the 1.5% PEI NFS membrane (0.34 $L/m^2.h$). Membrane fouling was suspected but was not confirmed.

Table 2. The characteristics of RAS from secondary clarifier of a local wastewater treatment plant

Parameter	Value
Total dissolved solids (TDS)	1295 mg/L
Total suspended solids (TSS)	4306 mg/L
NH_4^+	65.231 mg/L
Mg^{2+}	56.005 mg/L
Cl^-	144.343 mg/L

The availability of appropriate FO membranes is crucial to the development of FO technology. Problems, such as high reverse solute diffusion and high concentration polarization (CP) are frequently encountered in FO processes.[18] Meanwhile, although FO has a lower membrane fouling propensity than the pressure-driven membrane processes, fouling is still the most severe problem adversely influencing FO performance. Many novel FO membranes obtained through the surface modifications on ready-made membranes have been developed in

recent years (see review by Xu et al.[18]). The work presented here adds to the body of work in attempt to develop a FO membrane that has high water flux, low reverse solute flux and high ammonia rejection. The modified membrane is far from ideal for ammonia concentration. We have not addressed the membrane fouling, which is a universal challenge in all membrane processes. The presence of positive charged groups on membrane surface may attract negatively charged molecules in wastewaters, which exacerbate the fouling propensity. Future work to further improve the surface hydrophilicity may further improve the membrane antifouling properties. The work presented here offers a potential new application of FO in converting ammonia from waste to resources.

4. Conclusions

- We have successfully grafted PEI as functional groups on PA TFC NF membranes using DCC intermediate, as demonstrated by Raman spectroscopy.
- Most of modified membrane maintained the uniform surfaces with minimal changes in surface roughness in comparison with the virgin membrane.
- The PEI grafted NFS membranes have higher IEP than virgin membrane due to increases in amine groups attached to the membrane surface.
- Most of the PEI grafted NFS membranes had lower water contact angles in comparison with the virgin NFS membrane, indicating hydrophilicity.
- The water flux of PEI modified membranes varied among different concentrations of PEI incorporation, with some having greater water flux than the virgin NFS membrane, while the fluxes were reduced for others.

- The reverse fluxes of the PEI-NFS membrane for Mg^{2+} and Cl^- ions were reduced in comparison with the virgin membrane.
- With consideration of the water fluxes, reverse solutes (Mg^{2+} and Cl^- ions) fluxes and ammonium rejection, the 1.5% and 3% PEI NFS are considered the best overall performer.
- Improvement of ammonium rejection and the reverse solutes (Mg^{2+} and Cl^- ions) fluxes by 1.5% PEI-NSF was also demonstrated using RAS of a local wastewater treatment plant .

Acknowledgements: Funding support for this research was partial provided by U.S./China Clean Energy Research Center for Water-Energy Technologies program (DE-IA0000018) to UCI. We would also like to express our gratitude towards the Orange County Sanitation District for their support of wastewater sample collection and monitoring data. We thank the facility directors at the Laser Spectroscopy and Optical Biological Core Facilities at the University of California, Irvine for their guidance of the spectroscopy and microscopy work.

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Table of contents entry:

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