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ARTICLE

Novel Chlorine Resistant Low-Fouling Ultrafiltration Membrane Based on a Hydrophilic Polyaniline Derivative

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We demonstrate that poly(n-2-hydroxyethyl aniline) (n-PANi), a derivative of polyaniline (PANi), provides an effective chlorine tolerant PANi-based ultrafiltration (UF) membrane. n-PANi was synthesized from its monomer via chemical oxidative polymerization. Unlike PANi, n-PANi can be dissolved in N-methyl-2-pyrollidone (NMP) up to 30 wt% to form a casting solution which is stable for months without the aid of an anti-gelling agent. Membranes formed from n-PANi show high resistance to chlorine, even when exposed to 250 ppm sodium hypochlorite for 30 days while PANi membranes completely lose their ability to reject bovine serum albumin (BSA, 6 nm) after 2 days. Spectroscopic studies indicate that the benzenoid groups in PANi membranes are oxidized while n-PANi membranes maintain their chemical structure. n-PANi membranes display high hydrophilicity with a contact angle of 36 degrees which contributes to their ultra-low adhesion of *E. coli*. Cross-flow fouling tests with 1.5 g/L BSA fouling solution reveal that n-PANi membranes are very low-fouling with only 11% flux decline and 91% flux recovery, superior to PANi and commercial Polysulfone (PSf) membranes.

Introduction

An abundant supply of fresh water is a fundamental requirement for municipal, industrial and agricultural use. However, rising populations and source contamination have exerted increasing stress on fresh water supplies. Along with pressure from stricter regulations for clean water, improvements in water treatment technology are critical to sustain future generations.[1,2]

Membrane-based filtration is the most important and widely used method for water purification due to its ability to effectively remove impurities in feed sources on a large scale. Generally, membranes can be categorized into four types: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) based on their pore size and ability to reject a variety of materials for different applications.[1]

Typical UF membranes have an average pore size of 10 nm[3]. In waste water treatment, ultrafiltration is used to reject pathogenic microorganisms such as viruses, bacteria, protozoa and other colloids[3] and can serve as a pretreatment step for desalination.[1,4] UF membranes are commonly used for separations in the chemical, pharmaceutical, food, and beverage industries, and are an integral component in blood dialysis.[3]

When a membrane is used for separation, the flux gradually decreases during operation as the membrane is fouled by inorganic particulates, organic matter and/or biological microorganisms.[1] The susceptibility to fouling by organic elements varies among different membrane materials due to hydrophobic interactions between the foulant and the surface of the polymeric membrane. Thus, membrane hydrophilicity has been linked to a membrane's propensity to foul, i.e. hydrophilic membranes generally foul less than hydrophobic membranes.[5,6] A more hydrophobic membrane allows foulants to adhere strongly via van der Waals interactions to the membrane surface that leads to irreversible membrane fouling.[7]

Chemical cleaning is typically used to remove biofilms and adsorbed organic material from the membrane surfaces. Cleaning treatments restore membrane performance to regain flux loss during operation due to membrane fouling. Common chemicals used for cleaning membranes include caustics,

oxidants/disinfectants, acids, chelating agents and surfactants.[8] Chlorine bleach (sodium hypochlorite), is popular in industry for its commercial availability, low cost and ability to effectively reduce fouling when added to the feed solution. Strong oxidants such as hypochlorite not only kill microorganisms, but also oxidize functional groups in natural organic matter into more water-soluble moieties, allowing the new species to be readily washed away during operation. However, strong oxidants simultaneously attack chemical bonds found within the polymeric membrane material, negatively affecting the membrane properties.[9-21]

Prior studies have suggested that chlorine cleaning of UF membranes often causes more harm than good.[15-19] Multiple cleaning treatments facilitate chain scission of the membrane polymer and deteriorates the mechanical strength of the membrane, leading to failure. Furthermore, these treatments can increase fouling due to changes in surface charge that increase interactive forces between the foulant and the membrane surface.[15] Similarly with polymeric reverse osmosis membranes, chemical attack by chlorine on polyamide RO membranes results in membrane failure with enhanced passage of salt and water.[20-24] In response, attempts have been made to modify membrane materials in order to impart resistance to chlorine degradation. Prior research has demonstrated that small molecules and polymers containing secondary arylamines (Fig. 1) undergo Orton rearrangements[23] when exposed to sodium hypochlorite, leading to chain scission. When n-substituted (tertiary) arylamine derivatives are used, Orton rearrangement is hindered and the small molecules and polymers exhibit higher chlorine tolerance than their di-substituted counterpart.[20-24]
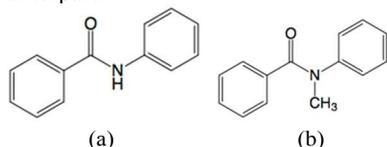

Fig. 1 A polyamide unit with a secondary amine (a) is more susceptible to chlorine attack than that consisting of tertiary amine (b).

Recently, conducting polymers and their derivatives have been extensively examined for their potential use in water treatment membranes due to their hydrophilic properties, thermal and chemical stability, low-cost, facile synthesis and straightforward modification via doping.[5,6,25-34] Polyaniline (PANi), one of the most widely studied conducting polymers, has been blended with the commercial UF membrane material polysulfone (PSf) to form composite UF membranes with enhanced hydrophilicity and permeability.[30-33] Pure PANi has also been used to form UF membranes; however, pure PANi membranes do not demonstrate sufficient protein selectivity for typical UF operation.[33] By adding a secondary amine such as 4-methylpiperidine (4-MP) into the PANi casting solution, the processability of PANi is improved, and casting solutions of higher concentration can be achieved to produce membranes with higher selectivity.[34] Unfortunately, the advantageous hydrophilicity of PANi is lost due to the remaining 4-MP in the resulting membrane, as indicated by NMR experiments. In another study, sulfonated PANi (SPANi) was blended with PSf at low loadings to form UF membranes which have shown excellent hydrophilicity and high flux restoration after cleaning only with water.[5]

Despite the improvements in hydrophilicity and performance, the redox properties of PANi causes the polymer to be highly susceptible to chlorine degradation. In its emeraldine base form, approximately half of the aryl rings in the backbone are benzenoid containing secondary amine groups that are vulnerable to attack by sodium hypochlorite.[20-24] In contrast, n-substituted PANi does not contain secondary amine groups. The reaction rate between hypochlorite and a primary/secondary amine is 5 orders of magnitude higher than the reaction between hypochlorite and a tertiary amine.[35] Thus, we believe n-substituted PANi is a suitable candidate for the fabrication of chlorine resistant UF membranes. Thus, our goal is to synthesize an n-substituted PANi-derived membrane material that possesses hydrophilic properties and chlorine resistance to both reduce the rate of fouling and tolerate chemical cleaning conditions.

Several types of n-substituted PANi derivatives have been reported in the literature.[36,40-43] Among these, n-alkyl PANi is the most common form. Because the addition of alkyl chains to the backbone increases hydrophobicity, we utilize a hydrophilic poly(n-2-hydroxyethyl aniline) (n-PANi) as a polyaniline derivative to fabricate UF membranes. The membranes' performance was tested before and after exposure to a sodium hypochlorite solution to evaluate the chlorine tolerance of the membranes. The polymeric materials were characterized with FT-IR, UV-vis and NMR to probe the mechanism associated with membrane degradation from chlorine exposure. Additionally, captive bubble contact angle measurements were employed to determine membrane hydrophilicity.

(n)   (b)
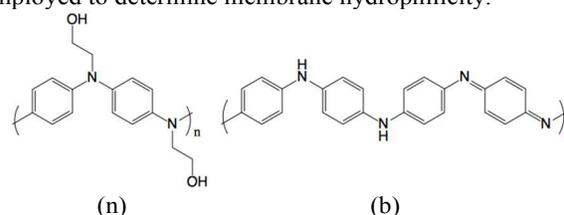
Fig. 2 The polymer structures of (a) n-PANi and (b) PANi.

Experimental

Materials

N-(2-hydroxyethyl) aniline, aniline, bovine serum albumin (BSA), N-methylpyrollidone (NMP), 4-methylpiperidine (4-MP), ammonium persulfate (APS), Escherichia coli (E. coli), Luria-Bertani (LB) broth and sodium hypochlorite solution (10%) were purchased from Sigma Aldrich. Hydrochloric acid, dimethyl sulfoxide (DMSO), sodium hydroxide pellets and sulfuric acid (90%) were purchased from Fisher Scientific. Dimethyl sulfoxide-d6 was purchased from Cambridge Isotope Laboratories. All materials were used as received.

Synthesis

n-PANi was prepared from n-(2-hydroxyethyl) aniline via chemical oxidative polymerization. The monomer and APS
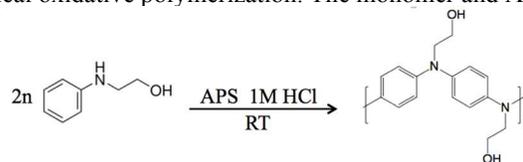
Fig. 3 Polymerization scheme for n-PANi.

were dissolved separately in 1 M HCl aqueous solutions. The solution of APS was added drop-wise at room temperature into the monomer solution under vigorous stirring. The reaction was allowed to proceed for 24 hours. n-PANi was purified from the

crude mixture via centrifugation at 3000 rpm for 5 minutes followed by dialysis using dialysis tubing with 12,000-14,000 MWCO (Fisherbrand) in a deionized (DI) water bath. The water bath was replaced with fresh DI water every two hours until the pH of the water bath remained neutral. The dark green polymer powder was isolated by removing the polymer dispersion from the dialysis bag and dried *in vacuo* at 60 °C overnight (yield = 65%).

PANi was prepared following the procedure described by Guillen *et al.*[33] It was synthesized via chemical oxidative polymerization from a 0.5 M solution of H_2SO_4 using APS as an oxidant with a 4:1 monomer to oxidant ratio. PANi was recovered with a microfiltration (0.45 μm membrane, Millipore) and washed with NaOH and DI water. The violet PANi dispersion was dried *in vacuo* at 60 °C overnight (yield = 25%).

Polymer solution preparation

An n-PANi casting solution was prepared by dissolving 30 wt% of n-PANi powder in 70 wt% NMP. The pure PANi casting solution was prepared following the procedure by Guillen *et al.*[34] by dissolving 21 wt% of PANi in 11.67 wt% of 4-MP and 67.33 wt% of NMP as a co-solvent. The weight percent of PANi and 4-MP were chosen to maintain 2 moles of 4-MP: 1 mole PANi base tetramer (0.547 g 4-MP: 1 g PANi tetramer).

Membrane fabrication

Membranes were hand-cast with a doctor blade (Gardco Adjustable Micrometer Film Applicator) from polymer solutions onto a non-woven polyester fabric (Hirose, Japan) using a blade height of 152 μm. As-cast solution films were immediately immersed in a DI water coagulation bath to induce polymer precipitation via non-solvent induced phase inversion.[44] The membrane films were left in the coagulation bath overnight before being transferred to a DI water bath and stored in a refrigerator at 4 °C.

Characterization

Membrane permeability and rejection tests were carried out using a dead-end stirred cell (Sterlitech) with a membrane area of 14.6 cm^2. Permeate flow rates were measured using a digital flow meter. Pristine membranes were compacted first using DI water at 1.38 bar (20 psi) until the flux decline was <5% over a 30 min time period. Membrane flux was measured under pressures of 1.38, 1.04, 0.69, 0.34 bar (20, 15, 10 and 5 psi). Pure water permeability data were determined by plotting the flux as a function of pressure. BSA (6 nm in diameter[33]) was used to evaluate the membrane rejection properties. Concentrations were determined using an Agilent 8453 UV-Visible Spectrophotometer. BSA rejection was calculated from

$$R = 1 - c_p/c_f,$$

where c_p is the BSA concentration in the permeate and c_f is that in the feed solution.

To evaluate chlorine tolerance, 250 ppm sodium hypochlorite solutions (pH = 8.5) were prepared by diluting a concentrated sodium hypochlorite solution with DI water. The concentration of free chlorine was measured using an HACH Pocket Colorimeter[TM] II chlorine test kit. N-PANi and PANi membranes were compacted as described above before being soaked in 250 ppm hypochlorite solution for different periods of time. Pure water permeability and BSA rejection were measured as described above for pristine membranes.

The molecular weight of as-synthesized n-PANi was measured using a Brookhaven NanoBrook 90Plus Molecular Weight Analyzer equipped with a 660 nm diode laser for light scattering experiments. A series of n-PANi/NMP solutions with different concentrations were made for the analysis. Scattered light intensities were measured at several angles for each of the solutions and the pure solvent. Molecular weight can thus be calculated based on the relationship between scattered light intensities and solution concentrations.[49,50]

Cross-sectional morphologies and surface images were taken using a JEOL JSM-6701F scanning electron microscope. Unsupported membrane samples were used for cross-sectional imaging. The membranes were prepared from polymer solutions cast unsupported on a glass plate followed by precipitation via non-solvent induced phase inversion in a DI water bath. The resulting unsupported membrane films were peeled off and dried *in vacuo* overnight at 60 °C. Membrane surface images were observed at 3,000× and 100,000× to visualize the pore size and porosity. In order to determine the chlorine damage on membrane morphology, n-PANi and PANi membranes were soaked in 250 ppm free chlorine for 2 days before drying. Cross-sectional and surface images of the pristine and chlorine exposed membranes were viewed at 600× magnification.

Fourier Transform Infrared Spectrometry (FT-IR) was conducted using a JASCO FT/IR-5300. Membrane samples were cut into 1 cm x 2 cm small rectangular pieces and dried *in vacuo* overnight before making measurements.

An Agilent 8453 UV-Visible Spectrophotometer was utilized for UV-Vis characterization with polymer powders using DMSO as a blank solvent. Polymer powders were chlorinated by being submerged in 250 ppm chlorine solution for 2 days before drying and dissolving in DMSO.

[1]H-Nuclear Magnetic Resonance (^{1}H-NMR) experiments were carried out in a Bruker Avance AV300 (300.1 MHz) instrument at room temperature. The unsupported membrane was grinded into powder with a mortar and pestle and dissolved in deuterated DMSO. The ^{1}H-NMR chemical shifts are reported relative to the deuterated DMSO solvent signal.

Membrane surface contact angle measurements were carried out with a KRÜSS DSA 10 goniometer. The captive bubble method was chosen instead over sessile drop method so that the membranes remain wet during the measurement without the change of morphology associated with drying.[45]

Bacterial attachment tests were performed on n-PANi and PANi membranes using *E. coli* as a model microorganism to evaluate bacteria deposition resistance. E. coli cell cultures were suspended in LB broth and incubated at 35 °C while shaken at 150 rpm for 24 hours in a New Brunswick Scientific I 24 Incubator Shaker. Cells were then harvested by centrifugation at 3800 × g for 8 min. After, the cells were diluted with fresh LB broth to a concentration of 4 x 10^7 cells/ml. Membrane coupons of approximately 1 cm^2 were incubated in E. coli suspension for 24 hours at 35 °C while shaken at 25 rpm followed by rinsing with fresh LB broth. Membrane coupons were then immersed and stained in SYTO 9 dye solution (live/dead Baclight Bacterial Viability Kit L13152, Molecular Probes) for 15 min. Images with bacteria deposition were taken using a fluorescence microscope (Olympus BX5) and a 4 × CCD camera (FVIEW-II, Soft Imaging System, USA).

A cross-flow system was used to determine the fouling behaviour of the membranes using the same method described by McVerry *et al.*[5] A 19 cm^2 cutout of each supported

membrane was placed in the cross-flow cell. A computer connected to a balance recorded the mass change of the permeate with time, enabling the flux to be monitored in real-time. The membranes were compacted using DI water at 16 psi until the flux stabilized. The flux was then normalized to 68 lmh (40 gfd) by manually reducing the operational pressure. Once stable, DI water in the feed tank was replaced by 1.5 g/L BSA solution to observe flux decline due to BSA fouling. The fouling test was continued for 25 min followed by flushing with DI water for 25 min.

Results and Discussion

N-PANi and PANi Processability

PANi is known to gel rapidly at relatively low solution concentrations, even as low as 5 wt%.[37] In order to achieve a
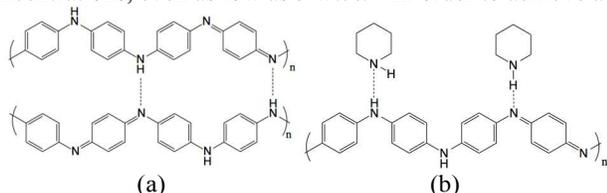
Fig. 4 (a) Gelling of PANi is caused by intermolecular hydrogen bonding. (b) 4-MP inhibits PANi from gelling by taking up some of the hydrogen bonding sites.

high concentration for casting highly selective membranes, secondary amines such as 4-MP have been used to prevent PANi solutions from gelling.[38,39] Unfortunately, the addition of 4-MP results in a loss of hydrophilicity.[34] Due to the aliphatic side chains in the polymer structure,[36,43] n-PANi derivatives are generally very soluble in common organic solvents such as NMP and DMSO. With regard to membrane casting, n-PANi can be readily dissolved in NMP at high concentration without gelation.

We found that n-PANi solution concentrations as high as 30 wt% can be achieved without gelation. n-PANi is comprised mostly of aniline rings in its benzenoid form with a flexible aliphatic side chain (Fig. 2 and 9) which increases the flexibility of the polymer backbone, compared to PANi. This flexibility prevents two adjacent polymer chains from forming a critical number of intermolecular hydrogen bonds that causes gelation. Additionally, steric hindrance from the long flexible side chains increases the distance between two adjacent polymer chains, which further suppresses intermolecular polymer interactions.

Permeability and Rejection Tests

To determine the flux and selectivity of the n-PANi membranes, pure water permeability and BSA rejection tests were performed. The % rejection was determined using the equation below:

$$R = 1 - A_p/A_f$$

where A_p and A_f are the UV-Vis absorbance of the permeate and feed solution at 280 nm, respectively. For comparison, a pristine PANi membrane was also tested. The n-PANi membrane exhibited a permeability of 86.8 lmh/bar (3.53 gfd/psi), while rejecting 65.8% BSA. The pure PANi membrane possesses a higher permeability (280.4 lmh/bar), but lower BSA rejection (12.9%). Membrane surface SEM images (Fig. 6a) show large pores on the PANi membrane surface. The pores are several hundred nanometers in diameter, comparable

to PANi membranes previously reported[33]. The large pores contribute to the relatively high permeability but low BSA rejection of the PANi membrane. At the same magnification, the n-PANi membrane surface appears to be defect-free and continuous. At 100,000×, slit-pores are observed on the n-PANi membrane surface (Fig. 6c). The image was converted to black and white (Fig. 6d) using NIH Image J software[33] in order to estimate the pore size. From these converted images, the slit-pores appear to be approximately 50 nm in length and 10 nm in width, manifesting the n-PANi membrane's higher BSA rejection.

Table 1 Permeability and BSA Rejection of Membranes Before and After being Soaked in 250 ppm Free Chlorine

	Pristine	Chlorine 1 d	Chlorine 2 d	Chlorine 30 d
N-PANi Permeability (lmh/bar)	86.9	103.3	100.6	108.7
N-PANi rejection (%)	65.8	62.9	75.7	70.2
PANi Permeability (lmh/bar)	280.4	642.1	1328	N/A
PANi rejection (%)	12.9	1.8	0	N/A

The n-PANi membrane was cast with a 30 wt% polymer solution (higher than that of PANi membrane at 21%) to increase the casting solution viscosity to make the solution suitable for casting. The lower viscosity is likely due to the lower molecular weight of the n-PANi. N-substituted aniline derivatives typically produce lower molecular weight polymers compared to PANi, due to increased steric hindrance[51]. To determine molecular weight, dynamic light scattering was used (DLS), giving a molecular weight for the synthesized n-PANi of 17.2 kDa, which is lower than the reported value for PANi[52]. In this case, molecular weight of the synthesized PANi could not be measured with DLS due to PANi's strong absorption at 660 nm, which is the wavelength of the DLS laser (see the later discussion of UV-Vis, Fig. 8). However, PANi synthesized by chemical oxidative polymerization typically produces polymers in the (20-40) kDa range.[33]

Generally, increased polymer concentration in a casting solution leads to higher polymer density at the nonsolvent interface[46] during the phase inversion process. Therefore the volume fraction of the polymer increases while the porosity decreases[44], resulting in lower permeability and higher rejection. To investigate changes in performance, surface and cross-sectional SEM images of membrane samples were taken. As can be seen in Fig. 6 (e) and (g), the morphology of the PANi membrane shows finger-like voids that extend across the entire span of the membrane. In contrast, the n-PANi membrane's finger-like voids extend only through the upper half of the membrane, indicating a denser morphology, consistent with its lower permeability compared to the PANi membrane.

To evaluate changes in chlorine tolerance based on chemical structure, PANi and n-PANI membrane coupons were exposed to sodium hypochlorite solutions for 2 days and the performance and rejection were examined. After soaking in the 250 ppm sodium hypochlorite solution, the permeability of the pure PANi membrane increased drastically from 280.4 lmh/bar to 1328.4 lmh/bar (Table 1). The BSA rejection of the pure PANi membrane also decreased significantly from 12.9% to 0 indicating that exposure to chlorine damaged the PANi membrane. The surface SEM image in Fig. 6j clearly shows the damage that the chlorine exposure causes to the membrane. The exposed PANi membrane possesses large defects in the surface. Chlorine also damages the interior structure of the PANi membrane, which appears to lose mass and thickness (Fig. 6f). On the other hand, the permeability of the n-PANi membrane changes only slightly from 86.9 lmh/bar to 100.6 lmh/bar upon chlorine exposure, with little change in BSA rejection. Fig. 6h and l indicate that the n-PANi membrane surface and interior structure are unaffected by chlorine exposure. It is also worth noting that there was visible bleaching of the PANi membrane sample upon exposure to the chlorine treatment (Fig. 5). Chlorine oxidizes the benzenoid groups (as discussed in the following section) and decreases the extent of conjugation across the polymer backbone. This phenomena reduces the absorption of photons giving rise to π-π* transitions, resulting in chemical bleaching.

	Before	After
n-PANi		
PANi		
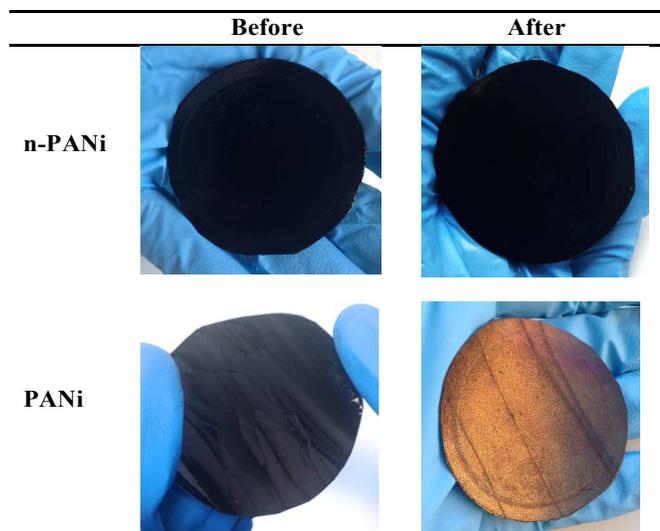
Fig. 5 Photos of PANi and n-PANi membranes before and after being soaked in 250 ppm free chlorine for 2 days.

During industrial operation, chlorine cleaning is performed either by backflushing with 2-8 ppm hypochlorite solution for 1 min or soaking in 20-400 ppm free chlorine for 1h periodically. The combined effect of chlorine oxidation can be expressed in a concentration × time manner.[15] Long-term chorine resistance of n-PANi membrane was tested by extending the soaking time in 250 ppm free chlorine solution to 30 days. Fresh hypochlorite solutions were prepared and exchanged every 2 days. At the end of the 30-day period, the membrane performance was evaluated. After 30 days, the n-PANi membrane maintained its pure water permeability of 108.7 lmh/bar and a BSA rejection of 70.2%, indicating outstanding long-term chlorine resistance. n-PANi is able to withstand at least 180,000 mg h/L of free chlorine exposure. Therefore, we believe n-PANi is a viable

candidate for long-term use in water treatment plants without failure due to chlorine degradation.
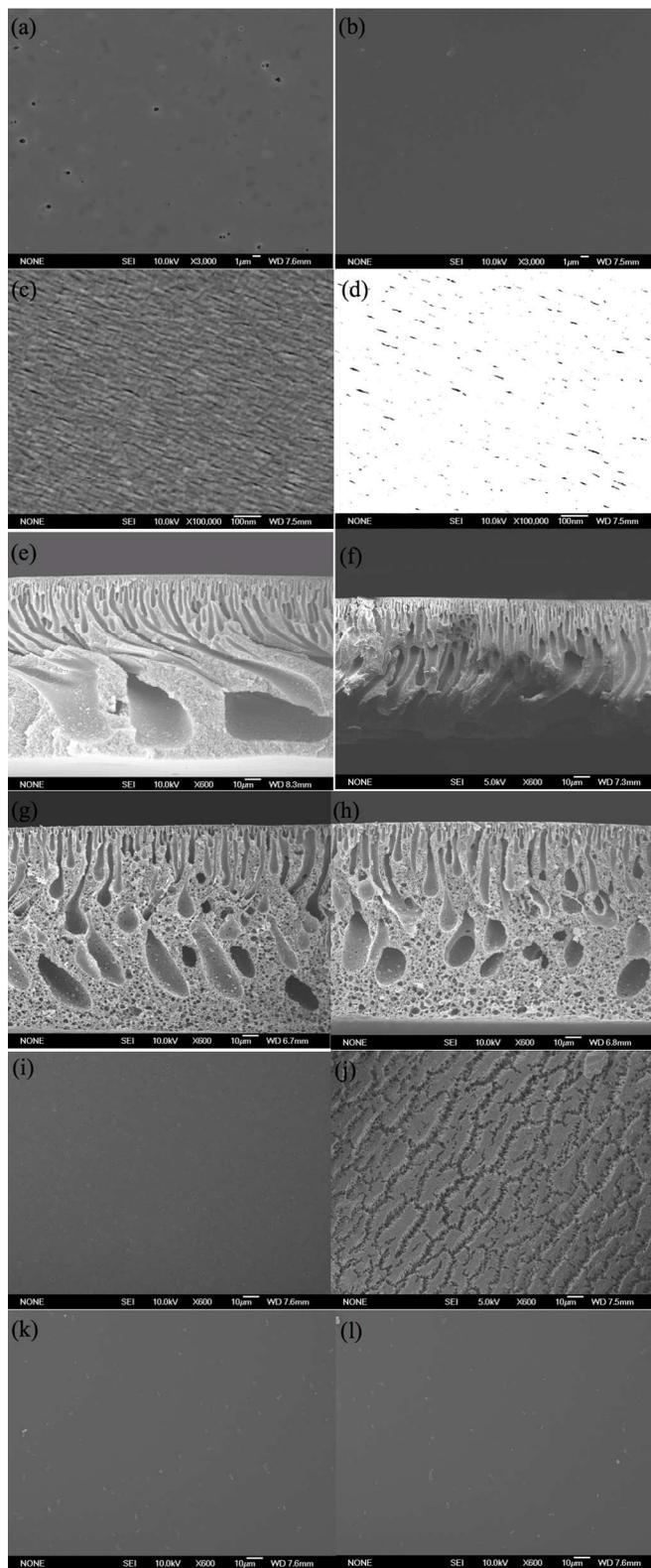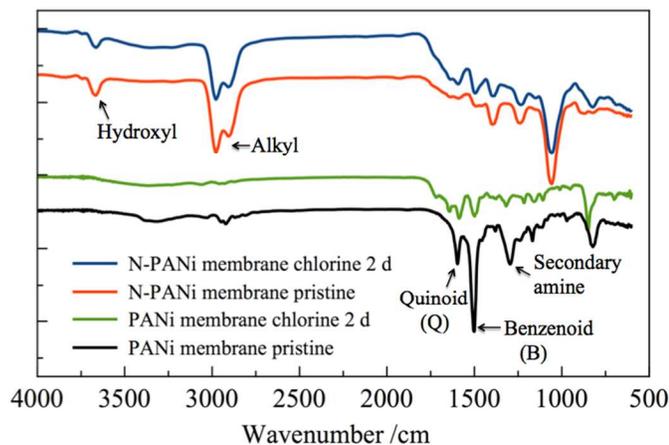

Fig. 6 SEM images of (a) a PANi membrane and (b) an n-PANi membrane surface at 3,000× magnification, (c) an n-PANi membrane surface at 100,000× magnification and (d) its black-

white picture after conversion using Image J software. Cross-sectional images of (e) pristine PANi membrane, (f) PANi membrane after chlorine exposure, (g) pristine n-PANi membrane and (h) n-PANi membrane after chlorine exposure at 600× magnification. Surface images of (i) pristine PANi membrane, (j) PANi membrane after chlorine exposure, (k) pristine n-PANi membrane and (l) n-PANi membrane after chlorine exposure at 600× magnification.

Spectroscopic Analysis

To probe redox chemistry induced by chlorine treatment, ATR-IR was employed. Upon examination of the benzenoid and quinoid moieties within the PANi and n-PANi backbones after chlorination, the differences in chemical structure are discernible (Fig. 7). In the PANi IR spectrum, the quinoid peak shifts from 1597 cm^{-1} to 1587 cm^{-1} and the benzenoid peak shifts from 1501 cm^{-1} to 1498 cm^{-1} upon chlorine exposure. However, the quinoid and benzenoid peaks of the n-PANi remain at 1591 and 1495 cm^{-1}, respectively, after being soaked in 250 ppm free chlorine for 2 days. Additionally, the intensity ratio of the quinoid group to the benzenoid group in the PANi membrane increases from 0.5 to 1 (Table 2). A decrease in the intensity of secondary amines, corresponding to a decrease in benzenoid rings, in the PANi membrane is also observed at
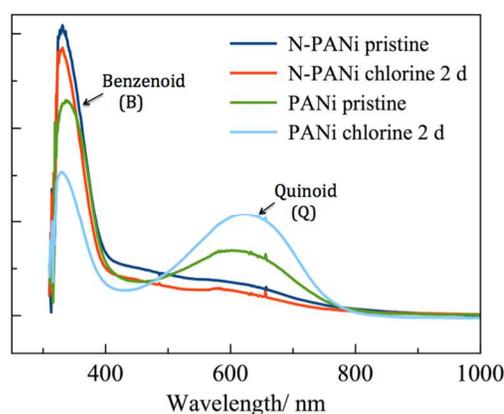
1270 cm^{-1}. The alkyl peak around 2900 cm^{-1} in the as-cast PANi membrane is indicative of remaining NMP and 4-MP within the film (also observed in the NMR spectrum in Fig. 9). After being exposed to 250 ppm free chlorine for two days, the alkyl peaks almost disappear due to the fewer available benzenoid units for NMP to bond to. These changes suggest that the benzenoid groups are oxidized by chlorine. In contrast, the n-PANi membrane remains unchanged upon chlorine exposure. The benzenoid:quinoid ratio is only slightly altered from 1.2 to 1.3 while the peak positions do not shift, indicating the polymer's tolerance to oxidation.

To further investigate benzenoid to quinoid oxidation from chlorine exposure, UV-Vis spectroscopy was utilized. In the UV-vis spectra, n-PANi absorbs in one region with a λ_{max} at 331 nm, corresponding to the benzenoid π-π* transition. For PANi, a separate peak appears at 601 nm, corresponding to the quinoid π-π*.[53] With chlorine exposure, n-PANi displays no apparent change in its UV-Vis spectrum. In contrast, the spectrum of PANi varies markedly upon chlorine exposure. A blue shift is observed for the benzenoid peak (338 nm → 329 nm) and a red shift is observed for the quinoid peak (601 nm → 624 nm) due to chain cleavage and chloride substition on the quinoid rings (Table 3). The intensity ratio of the quinoid to benzenoid peak also increases, which is consistent with the IR spectra, further indicating benzenoid ring oxidation reactions.

Fig. 7 FT-IR spectra of membranes before and after being soaked in bleach containing 250 ppm free chlorine. The small peak at 875 cm^{-1} for n-PANi pristine membrane is due to the choride counterion on doped n-PANi membrane. After n-PANi membrane is soaked in basic sodium hypochorite solution, n-PANi is dedoped, demonstrated by the disappearance of the chloride counterion peak.

Table 2 The FT-IR Benzenoid (B) and Quinoid (Q) Peak Positions and Intensity Ratios for N-PANi Membranes

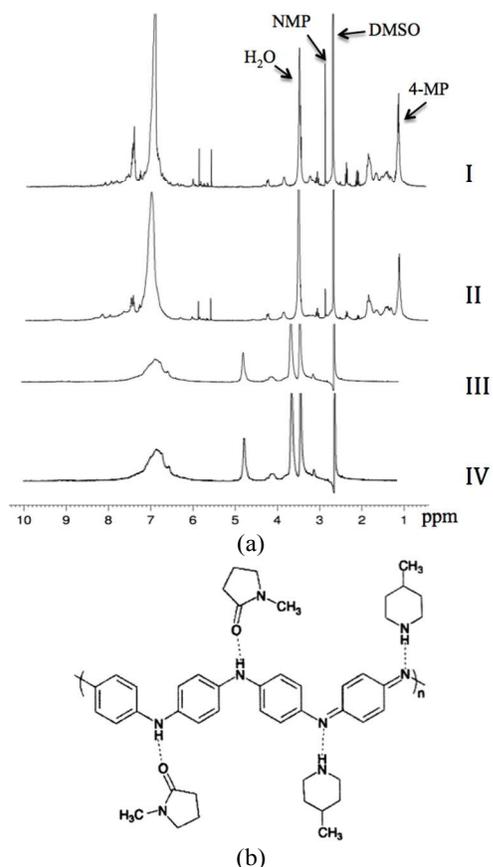|	Pristine	Chlorine 2 d
N-PANi B/cm^{-1}	1495	1495
N-PANi Q/cm^{-1}	1591	1591
N-PANi Q/B	1.2	1.3
PANi B/cm^{-1}	1501	1498
PANi Q/cm^{-1}	1597	1587
PANi Q/B	0.5	1.0

Fig. 8 UV-Vis spectra of membranes before and after being soaked in bleach containing 250 ppm of free chlorine.

Table 3 The Benzenoid (B) and Quinoid (Q) Peak Positions and Ratios for N-PANi and Pure PANi Membranes

	N-PANi B/nm	PANi B/nm	PANi Q/nm	Q/B
Pristine	331	338	601	0.33
Chlorine 2d	331	329	624	0.71

To determine chemical changes to the polymers, ^{1}H-NMR spectroscopy experiments were conducted on representative samples of the PANi and n-PANi polymers, before and after chlorine exposure (Fig. 9). The NMR spectra of the PANi membrane indicates that both NMP and 4-MP remain in the membrane after the phase inversion process with thorough rinsing. After exposure to chlorine, NMP is partially removed from the membrane. NMP interacts with the PANi backbone via hydrogen bonding[34] as depicted in Fig. 9 (b). As mentioned above, the decreased number of benzenoid rings in the backbone (after oxidation) removes hydrogen bond sites for the

NMP to interact with. In the spectrum for n-PANi, NMP is not present. Due to the presence of long n-alkyl side chains, the NMP solvent cannot interact strongly with the n-PANi backbone, and is removed during rinsing after the phase inversion process. Additionally, there is no visible change upon chlorination, manifesting the chlorine stability of the n-PANi membranes.


Fig. 9 (a) NMR spectra of I. pristine PANi membrane; II. PANi membrane soaked in 250 ppm free chlorine for 2 days; III. pristine n-PANi membrane; IV. n-PANi soaked in 250 ppm free chlorine for 2 days and (b) a schematic representation of the PANi/4-MP/NMP complex formed by hydrogen bondings[34].

Hydrophilicity and Fouling Behavior

To determine membrane hydrophilicity, captive bubble contact angle measurements were conducted. The n-PANi membrane exhibits an observed contact angle of 36.0±0.8° indicating its increased hydrophilicity compared to a PANi membrane (CA=52.8±2.3°). Bacterial attachment test results are shown in Fig. 10 with green fluorescence representing *E.* colonies adhered to the membrane surface. It is evident that n-PANi membranes are less prone to fouling compared to PANi membranes. This is in agreement with n-PANi's lower water contact angle values, i.e. higher hydrophilicity, which suppresses the undesirable hydrophobic interactions between microorganisms and the membrane surface. A hydrophilic surface is able to form a hydration layer which prevents foulants from absorbing onto the surface.[47,48]
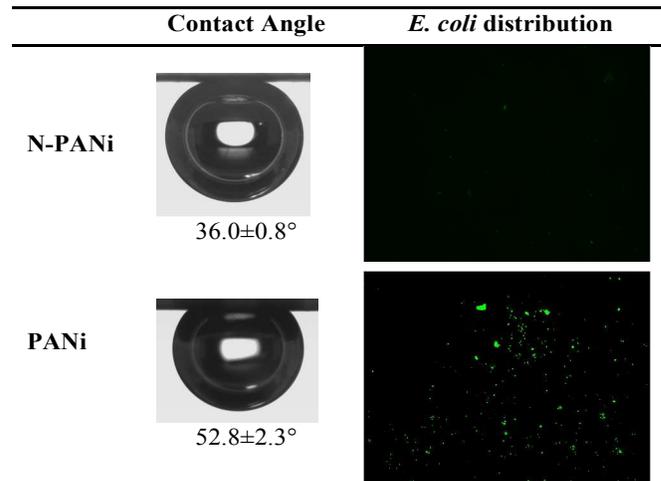
Fig. 10 Contact angles of n-PANi and PANi membranes and their *E. coli* adhesion test microscopic images.
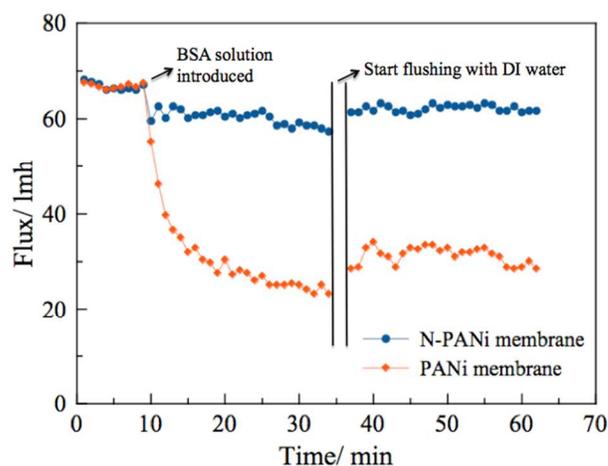
Fig. 11 Flux decline and recovery results for membranes fouled by 1.5 g/L BSA solution before being washed with DI water.

The antifouling properties of n-PANi membranes were further investigated using a cross-flow fouling test (Figure 11). After 10 min of stable flux, the feed was switched to a 1.5 g/L BSA solution. As soon as the BSA solution was introduced, there was a sudden decrease in flux caused by membrane fouling. The PANi membrane lost 63% of its initial flux due to fouling and only regained 44% of its initial flux when the feed was switched back to DI water after 35 min. The n-PANi membrane exhibits greater fouling resistance than the PANi membrane, only losing 11% of its initial flux from exposure to the BSA solution, while regaining 91% of its initial flux when rinsed with DI water. It's also worth noting that McVerry *et al.*[5] performed similar testing on a polysulfone membrane in which the same fouling technique was applied, and a commercial polysulfone membrane exhibited a greater amount of fouling with 50% flux decline after 10 min of fouling and 62% flux recovery after flushing with DI water. Therefore, n-PANi has proven to be a promising new membrane material due to its outstanding ability to effectively mitigate fouling.

Conclusions

We have successfully fabricated n-PANi chlorine resistant UF membranes with enhanced hydrophilicity. Due to the n-

substitution on the PANi backbone, the n-PANi polymer membranes can withstand exposure to 250 ppm free chlorine for as long as 30 days without showing any significant degradation in permeability or BSA rejection. In comparison, native PANi membranes completely lose its membrane integrity and ability to reject BSA after being soaked in 250 ppm free chlorine for just 2 days. Additionally, n-PANi membrane shows less bacterial adhesion and much lower BSA fouling during cross-flow operation compared with a PANi membrane. We believe n-PANi membrane is an exceptional candidate for UF applications with better fouling resistance, improved membrane longevity and reduced operational costs.

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Notes and references

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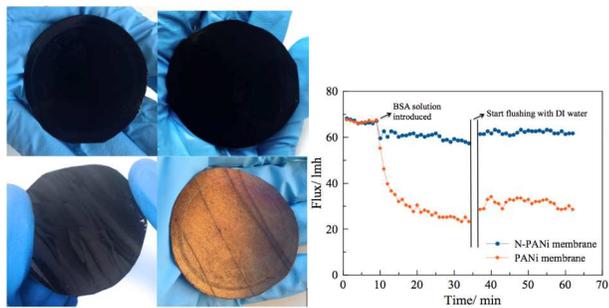
N-PANi, an outstanding candidate for making chlorine tolerant antifouling ultrafiltration membranes.