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Facile Grafting of Zwitterions onto the Membrane Surface To Enhance Antifouling Properties for Wastewater Reuse

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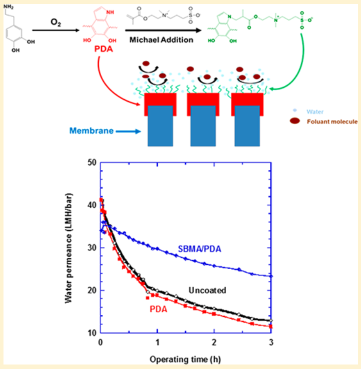
Ⓢ *Supporting Information*



ABSTRACT: Polymeric membranes for wastewater reuse are often fouled by suspended solids and dissolved organic matters, resulting in a dramatic decrease in water flux. Fouling can be mitigated by enhancing hydrophilicity of the membrane surface to avoid favorable interactions between the membranes and foulants. However, the modification of the membrane surface is often complicated and difficult to integrate into industrial membrane production processes. Herein we demonstrate a facile one-step coating of superhydrophilic zwitterions on the surface of ultrafiltration (UF) membranes by codepositing dopamine and sulfobetaine methacrylate (SBMA). In the presence of oxygen, dopamine forms polydopamine (PDA) adhering onto the membrane surface and anchors SBMA via Michael addition to form a robust thin superhydrophilic layer, as confirmed by contact angle measurement and X-ray photoelectron spectroscopy (XPS). The modified UF membranes demonstrate up to 80% higher water flux than the uncoated ones, when tested with water containing bovine serum albumin (BSA) as a model foulant in a crossflow system. This facile approach of membrane modification is also adapted for postmodification of a commercial nanofiltration (NF) membrane module, which demonstrates superior antifouling properties when tested with real wastewater at a wastewater treatment plant.

1. INTRODUCTION

Polymeric membranes have been widely used for wastewater treatment due to high energy-efficiency, small footprint, simplicity, and low cost.[1−3] Membranes can permeate pure water for reuse and reject contaminants such as suspended solids and dissolved organic matters. However, the contaminants can be adsorbed onto the membrane surface (i.e., fouling), due to their favorable interactions with the membrane surface, which would dramatically decrease water flux and thus increase the membrane area required and the cost of wastewater reuse.

An effective strategy to mitigate membrane fouling is to chemically modify the membrane surface with antifouling materials via direct thin film coating, monolayer self-assembling, and polymeric grafting.[2,4−12] These hydrophilic antifouling materials form hydration layers on the membrane surface, which act as a physical and energy barrier for contaminants to aggregate onto the membrane surface. The thin film coating of a hydrophilic polymer is particularly interesting because the coating can be easily implemented into current membrane production processes.[4,5,7,9,13−23] For example, bioinspired dopamine can adhere to a variety of surfaces and form hydrophilic polydopamine (PDA) in the presence of oxygen, rendering it good antifouling properties.[3,24−31] While the mechanism of PDA formation and the structure of PDA are still under debate, the hydroxyl and amines are ascribed to the strong adhesion toward the surface,[32−34] and the bulk PDA forms through covalent bonds or noncovalent bonds (such as charge transfer, $\pi-\pi$ stacking, and hydrogen bonding).[3,9,35]

Zwitterionic materials containing both positively and negatively charged groups with net neutral charge exhibit excellent antifouling properties, due to the strong surface hydration through electrostatic interactions.[36−46] Different zwitterionic polymers such as poly(sulfobetaine methacrylate) (PSBMA) and poly(carboxybetaine methacrylate) (PCBMA) were used to modify the membrane surface by coating or grafting to increase surface hydrophilicity.[47−57] However, these approaches often involve complicated procedures to deposit the thin zwitterion layers on top of the membranes, which may not be well-integrated into industrial membrane production processes. Another great challenge in using nonfouling and thus nonsticking zwitterions is to achieve long-term stability for

Received: June 9, 2017
Revised: July 17, 2017
Accepted: July 22, 2017
Published: July 23, 2017

ACS Publications

DOI: 10.1021/acs.iecr.7b02378
Ind. Eng. Chem. Res. 2017, 56, 9202−9212

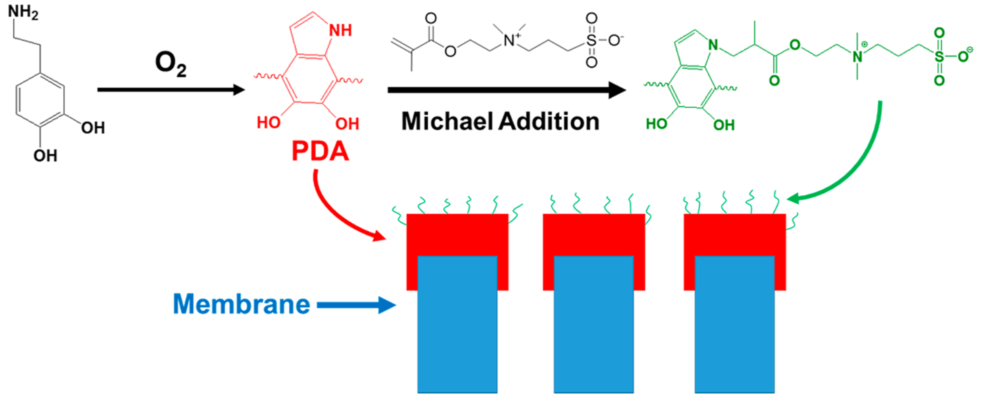


Figure 1. Simplified illustration of surface modification of UF membranes by one-step codeposition of PDA and SBMA to graft the zwitterions on the membrane surface with simplicity and good long-term stability.

membranes during operation, given their high solubility in water.

Herein, we demonstrate a new route of facile one-step membrane surface modification by synergistic codeposition of PDA and zwitterions functionalized with methacrylate groups such as sulfobetaine methacrylate (SBMA), which addresses both challenges of simplicity in modification and the long-term stability of zwitterions grafted on the membrane surface. As shown in Figure 1, when exposed to oxygen, dopamine forms a layer of PDA adhering to the membrane surface.[4,16,58] The amine groups in the bulk PDA layer randomly react with the methacrylate groups through Michael addition and thus covalently anchor the superhydrophilic SBMA onto the membrane surface, and the zwitterions in the SBMA can extend to the water due to the favorable electrostatic interactions,[9,59,60] leading to robust antifouling properties with long-term stability. This proposed surface modification occurs in the aqueous solution at room temperature, and thus it can also be applied as postmodification for membrane modules *in situ*.

Our one-step approach vastly differs from other surface modification procedures reported in the literature, where PDA was also used as bioglue to coat zwitterionic materials.[46,60−64] For example, TiO_2 substrates can be coated in two steps with dopamine first and then SBMA via the aza-Michael reaction.[60] One-step codeposition of PDA and zwitterionic polymers such as PSBMA[63] and poly(methacryloyloxyethyl phosphorylcholine) (polyMPC)[46,64] have been used to increase surface hydrophilicity. PDA interacts with charged groups to anchor the zwitterionic polymers onto the surface. However, there is no strong chemical bonding between PDA and zwitterionic materials.

In this study, we demonstrate the one-step coating of PDA and SBMA on three different commercial UF membranes to show the versatility of the approach, i.e., poly(ether sulfone) (PES-2) with nominal molecular weight cutoff (MWCO) of 4 kDa, polyacrylonitrile (PAN-50) with MWCO of 75 kDa, and polysulfone (PSf-100) with MWCO of 100 kDa. The effect of dopamine and SBMA content in the coating solutions and coating time on the coating layer thickness, surface hydrophilicity, and pure water flux are studied. The effectiveness of this surface modification to improve long-term water flux is evaluated using cross-flow filtration tests with water containing bovine serum albumin (BSA) as a model foulant. This approach was further applied to modify a commercial NF membrane module, which was then evaluated in a pilot study using real wastewater at a wastewater treatment plant. The work provides a new platform for facile and robust surface modification to improve membrane antifouling properties.

2. EXPERIMENTAL SECTION

2.1. Materials. Dopamine hydrochloride, Trizma hydrochloride (Trizma-HCl), BSA, SBMA, and phosphate buffered saline (PBS) were purchased from Sigma-Aldrich (St. Louis, MO), and ethanol was purchased from Fisher Scientific (Pittsburgh, PA). UF membranes of PES-2 and PAN-50 were provided from Sepro Membranes, Inc. (Oceanside, CA), and PSf-100 was obtained from Alfa-Laval Inc. (Warminster, PA).

2.2. Membrane Pretreatment and Surface Modification. Before surface modification, the membranes were pretreated to remove the additives such as glycerin inside the pores, which were used to preserve pore structures.[65] The membrane sheets were first soaked in ethanol for 24 h with the active side facing downward. Second, the sheets were rinsed under running ultrapure water, and then they were soaked in ultrapure water for 24 h before testing.

Coating solutions containing SBMA and/or dopamine with specific concentrations were prepared with a pH value of 8.5 by adding 430 mg of Trizma-HCl salt in 100 mL of pure water.[4] A membrane sheet was fixed on a plastic plate with the active side facing up. The solution was poured onto the active side of membrane, which was left on a rocking platform shaker (VWR International, Radnor, PA) to provide sufficient oxygen for PDA to form on the membrane surface. The treated sample was rinsed under running ultrapure water and soaked in ultrapure water overnight to remove any unbounded PDA and SBMA.

2.3. Contact Angle Measurements. The hydrophilicity of uncoated and coated membranes was examined using a Ramé Hart contact angle goniometer (Succasunna, NJ) through two different methods (i.e., sessile drop and captive bubble method). For the sessile drop method, water drops with the volume of 10 μL were injected onto the dried membrane surface. For the captive bubble method, membrane samples were placed on a sample holder with the active surface facing downward.[17] The sample holder was then submerged in a plastic transparent environmental chamber containing ultrapure water. Drops of *n*-decane (approximately 1 μL) were dispensed onto the membrane surface and left undisturbed for 2 min to ensure stabilization of the droplets. For both techniques, the values were taken as an average of at least five points.

2.4. Thickness Measurements. The thickness of coating layers (PDA or SBMA/PDA) on thin films of PSf was

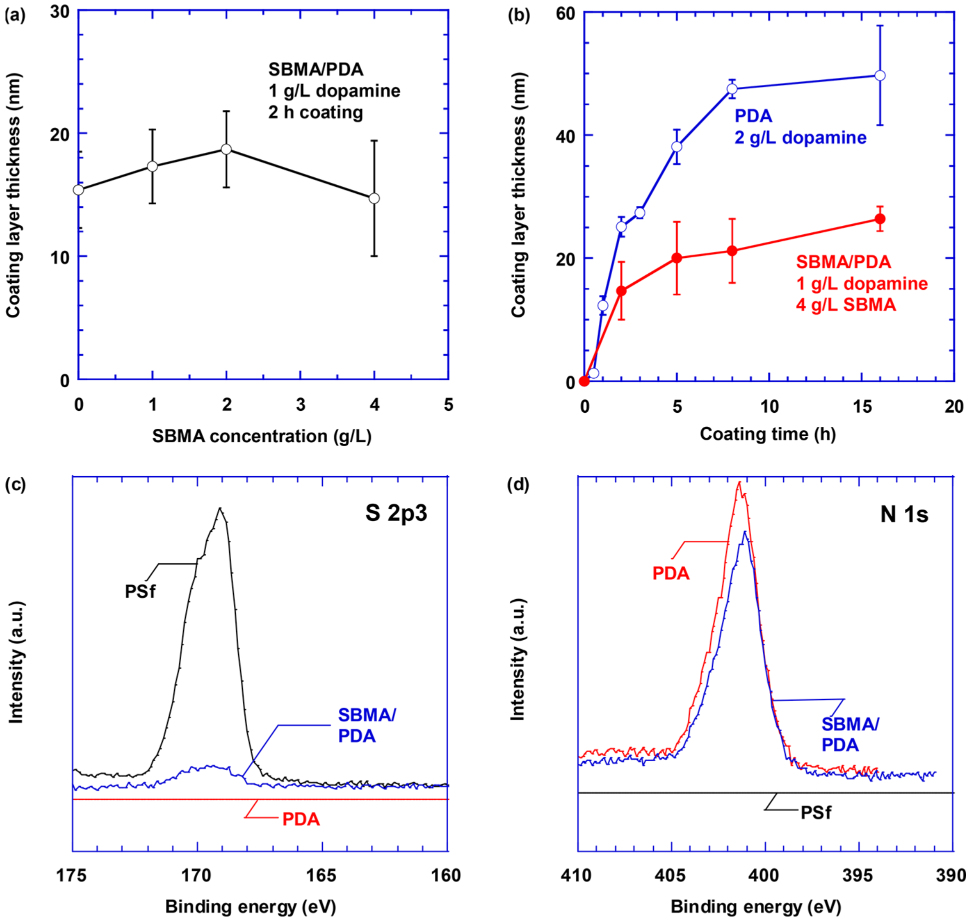


Figure 2. (a) Effect of SBMA content on the layer thickness at 1 g/L dopamine and 2 h of coating; (b) effect of coating time on the layer thickness when coated with dopamine at 2 g/L and SBMA/PDA at 1 g/L dopamine and 4 g/L SBMA; and comparison of XPS spectra of (c) S 2p3 and (d) N 1s for a PSf thin film, a PDA coated PSf with 2 g/L dopamine for 8 h, and a SBMA/PDA coated PSf film with 1 g/L dopamine and 4 g/L SBMA for 8 h.

determined using a Filmetrics F20 thin film measurement instrument (Filmetrics, Inc., San Diego, CA). First, a solution containing 3% PSf in cyclopentanone was prepared and coated onto a silicon (Si) wafer using a spin coater at a speed of 500 rpm for 3 s and then 5000 rpm for 1 min. After drying, the PSf film obtained has a thickness of 100−120 nm. Second, the film was coated using PDA or SBMA/PDA using the same procedure as described above. The thickness of the film was remeasured using the F20, and the increased thickness after the coating is ascribed to the coating layer. In fitting the F20 curves, refractive index values of 1.633, 1.6, and 1.374 are used for PSf,[66] PDA,[67] and SBMA,[68] respectively. For the SBMA/PDA coating, an additive model is used to estimate the refractive index.

2.5. X-ray Photoelectron Spectroscopy (XPS). XPS analysis (PHI 5600ci, Physical Electronics, Inc., Chanhassen, MN) was used to investigate the chemical characteristics of PDA and SBMA coated samples. The XPS instrument used monochromatic Al Kα X-rays, and the pass energy of the analyzer was 58.7 eV. Charge neutralization was used to minimize the effects of sample charging. Percentages of elemental composition are calculated from the relative areas of component peaks. The analysis was performed at 3 different regions for each sample to confirm the uniform coating.

2.6. Scanning Electron Microscopy (SEM). To investigate the surface morphology of uncoated and modified membranes, a sputtering coating apparatus was used to coat a thin gold layer onto the samples. The surface morphology analysis was then conducted using focused ion beam-SEM (FIB-SEM, Zeiss Auriga, Germany).

2.7. Pure Water Flux Measurement. The pure water flux through membranes was determined utilizing dead-end permeation cells (Sterlitech Corp., Kent, WA).[40,69] A membrane sample of 11.3 cm^2 was installed in the cell. The upstream chamber was filled with Milli-Q water and then applied with nitrogen at 30 psig. The permeate water was collected in a beaker, and the weight was recorded over time. The water permeance (A_W, L/m^2 h bar or LMH/bar) can be calculated using eq 1[40,69]

$$A_W = \frac{1}{\Delta p \cdot A_m \cdot \rho_W} \frac{dm}{dt} \tag{1}$$

where Δp is the pressure difference across the membrane (bar), A_m is the membrane area (cm^2), ρ_W is the water density (g/cm^3), and dm/dt (g/h) is the weight increase of the permeated water over time. For each membrane, six samples were tested, and an average permeance value is reported.

2.8. Crossflow Tests for Membranes. A custom-built crossflow filtration system was used to determine the water permeance over time to evaluate the antifouling properties. The system has three filtration cells in-series with a membrane surface area of 19.4 cm^2. A peristaltic pump (Cole Parmer,

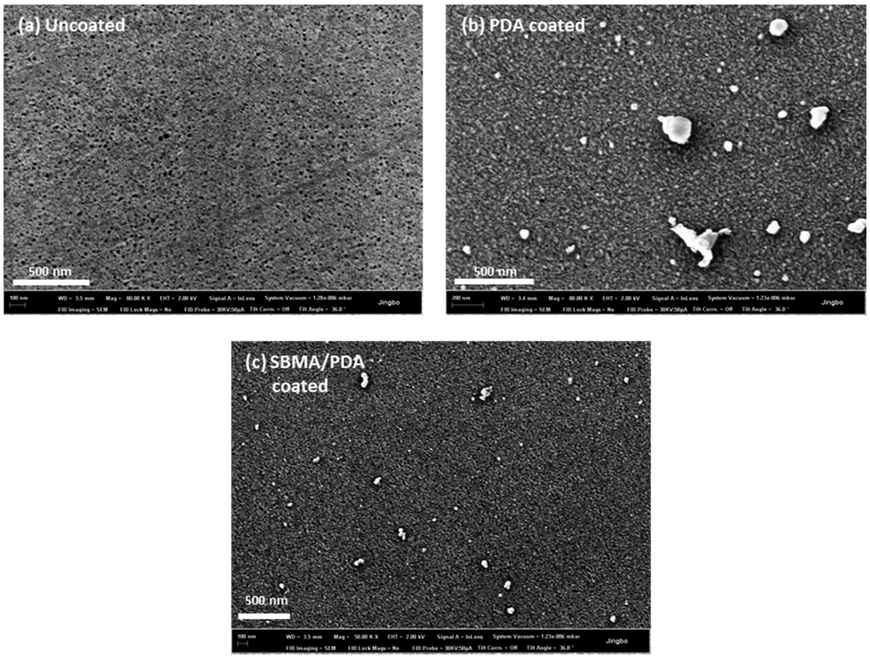


Figure 3. SEM characterization of the surface for (a) an uncoated PAN-50, (b) a PDA coated one (at 2 g/L dopamine), and (c) a SBMA/PDA coated one (at 1 g/L dopamine and 4 g/L SBMA). The coating time was 8 h.

USA) was used to provide a feed flow rate of 0.9 L/min at 30 psig (with a Reynolds number of about 1000), and the permeate was at atmospheric pressure. BSA was used as a model foulant, and PBS was used to obtain a pH of 7.4.

2.9. Module Modification and Field Test. A commercial polyamide-based nanofiltration (NF) membrane module (2.5-in. in diameter and 40-in. in length) (Applied Membranes, Inc., Vista, CA) was modified using our approach to enhance the antifouling property. First, the module was wet by circulating water continuously for 1 h from a beaker containing water using a peristatic pump. Second, a solution containing 8 g/L SBMA and 2 g/L dopamine was circulated in the feed channel of the module for 1 h. Third, the module was washed with deionized water for 1 h and then filled with deionized water for use.

The NF modules were tested in a mobile unit equipped with a drum containing secondary effluent wastewater at a wastewater treatment facility. The unit was operated in a batch mode with a feed pressure of 150 psig, and the original wastewater contained about 1,000 ppm total dissolved salts (TDS). The permeated water was released after the measurement of the contents of salt and organic matters, and the rejected water was recycled back to the drum. During the treatment, the content of the contaminants in wastewater increased with time. Fresh wastewater was added regularly to replenish the drum.

3. RESULTS AND DISCUSSION

3.1. Study of Coating Layers on Dense PSf Thin Films.

Figures 2a and 2b present the effect of the coating solution composition and coating time on the layer thickness on a dense film of PSf (~100 nm). The use of PSf dense films allows the direct determination of film thickness using an ellipsometer or Filmetrics F20, while these techniques cannot be used to determine the thickness of the coating layer on porous membranes. In this study, PSf dense film is also used as a marker for UF membranes including PSf, PES ,and PAN with an assumption that the PDA layer thickness is independent of the substrate chemistry.[16]

As shown in Figure 2a, when coated with 1 g/L dopamine for 2 h, the PDA layer has a thickness of 15 nm, which is lower than that from the solution containing 2 g/L dopamine (25 nm, cf. Figure 2b). On the other hand, increasing SBMA content (from 0 to 4 g/L) in the coating solution has a negligible effect on the thickness of the SBMA/PDA layer, considering the error bars. This result suggests that the PDA formation may be a much more rapid process than the Michael addition reaction between PDA and SBMA, and thus, the reaction of SBMA and PDA may occur in the top layer of the coating, as illustrated in Figure 1.

As shown in Figure 2b, increasing the coating time increases the thickness of the coating layer (PDA or SBMA/PDA) before leveling off, which is consistent with other studies of the PDA coating.[16] For example, after 10-h coating using 2 g/L dopamine, the PDA thickness is 48 nm in this study, which is very close to the value of 45 nm reported.[16] The coating layers of SBMA/PDA are thinner than those of PDA, because of the lower dopamine content (1 g/L) in the solution for the SBMA/PDA coating than that for PDA coating (2 g/L).[34,70,71] On the other hand, SBMA does not directly attach to the membrane surface, due to the lack of specific interaction. For example, when the coating solution contains 4 g/L SBMA without dopamine, there is no thickness change for the PSf thin film after 2-h coating.

XPS was used to determine the elements (sulfur, *S*, and nitrogen, *N*, in this study) on the surface to confirm the coatings. PSf films show *S* element but no *N* element. Figure 2c demonstrates the successful coating of PDA on PSf, as indicated by the complete disappearance of *S* element. On the other hand, the SBMA/PDA coating exhibits low content of *S* element, suggesting the Michael addition occurring on the surface and the successful coating of SBMA on PDA layers.[60] As shown in Figure 2d, the PDA coating significantly increases *N* content, while the coating of SBMA/PDA slightly decreases

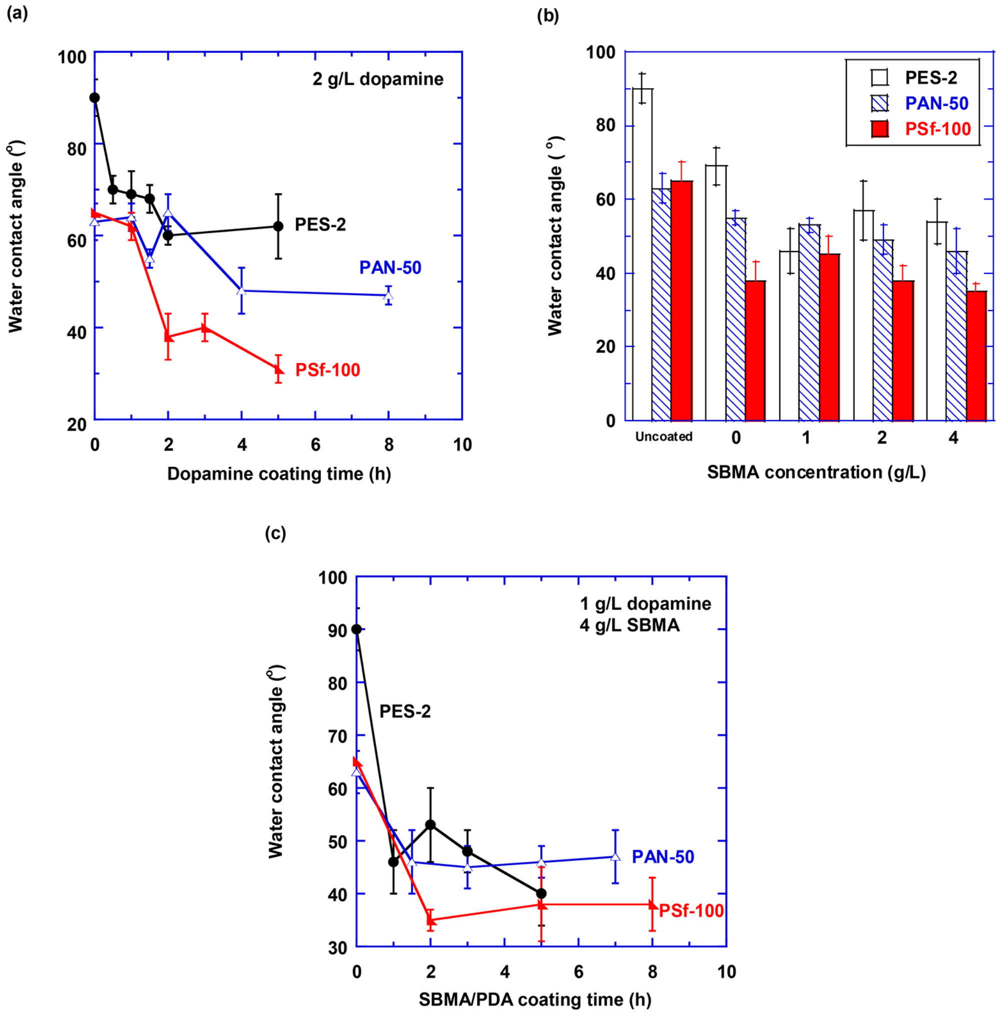


Figure 4. Effect of (a) dopamine coating time, (b) SBMA concentration in the coating solution containing 1 g/L dopamine, and (c) SBMA/PDA coating time on water contact angles of UF membranes. For (a) and (b), the PDA only coating was achieved using 2 g/L dopamine, and the deposition time of PES-2, PAN-50, and PSf-100 was 1, 1.5, and 2 h, respectively.

N content, since SBMA has lower *N* content than PDA. The molar percentage of SBMA is estimated to be 7% and 12% in the SBMA/PDA layer based on the concentration of the *N* and *S* element, respectively.

The Michael addition reaction may occur in the solution between SBMA and dopamine or in the coating layer between SBMA and PDA. To verify the possibility of the former route, we have used ^{1}H NMR to study the solution before the coating. We dissolved 4 g/L SBMA and 2 g/L dopamine in D_2O containing Trizma-HCl salt to provide a pH value of 8.5. The solution was kept in nitrogen for 2 h before the ^{1}H NMR test. The absence of oxygen prevents the dopamine polymerization, and the use of 2 h is consistent with the typical SBMA/PDA coating on membranes. There were no new peaks observed for the SBMA/dopamine solution, indicating that there was no detectable reaction of SBMA and dopamine in the solution. Therefore, during the membrane surface coating of SBMA/PDA, the dopamine is expected to form PDA first before the grafting of SBMA with PDA.

3.2. SEM Analysis. Figure 3 compares the PAN-50 surface before and after the modification characterized using SEM. The coating of PDA and SBMA/PDA decreases the pore size and results in the formation of aggregates. The aggregates are generally smaller for the SBMA/PDA coating than those from the PDA modification, due to the lower dopamine content in the solution for SBMA/PDA coating (1 g/L) than that for the PDA coating (2 g/L). These behaviors have also been reported for the surface coating with dopamine and zwitterionic polymers such as polyMPC/PDA[64] and PCBMA/PDA.[72] Smaller aggregates of the SBMA/PDA surface also suggest a smoother surface than that coated with PDA only.

3.3. Effect of Coating on Hydrophilicity of the Membrane Surface. Figure 4a shows the effect of dopamine coating time on the water contact angle of the membrane surface determined using the sessile drop technique. With the increase of dopamine coating time, the water contact angle initially reduces, indicating a significant increase in surface hydrophilicity. Further increase of coating time has a minimal effect on the water contact angles. These results are consistent with earlier studies of PDA coating on membranes based on PSf and PES,[16,73] because the contact angles are mainly determined by the hydrophilicity of the PDA layer and may be partially influenced by the substrate (or membrane materials).

Figure 4b exhibits that the introduction of SBMA in the coating solutions decreases the water contact angle for PES-2 and PAN-50, indicating the improved hydrophilicity derived from zwitterions. For example, this decrease was from 69° ± 5° to 46° ± 6° for PES-2 (as the SBMA content increased from 0 to 1 g/L) and from 55° ± 2° to 46° ± 6° for PAN-50 (as the SBMA content increased from 0 to 4 g/L). On the other hand, the addition of SBMA seems to have minimal impact on the water contact angles for PSf-100. Additionally, the pendant drop method was applied to determine the surface hydrophilicity of the membranes. This method mimics the membrane operation and uses *n*-decane as the probe where a lower contact angle indicates greater hydrophilicity.[17] The PDA and SBMA/PDA coating decreases the contact angle from 75° ± 3° to 53° ± 2° and 45° ± 3° in PSf-100, respectively, indicating the improved hydrophilicity from the zwitterions. Similar trends were also observed for PES-2 and PAN-50 membranes. The PDA and SBMA/PDA coating decreases the contact angle from 101° ± 5° to 66° ± 5° and 48° ± 5° in PES-2 and from 73° ± 2° to 50° ± 3° and 39° ± 2° in PAN-50, respectively.

Figure 4c shows that short deposition times (1−2 h) of SBMA/PDA are sufficient to enhance the membrane surface hydrophilicity. Further increase in the coating time has a minimal effect on the surface hydrophilicity. This trend is consistent with that for the PDA coating (cf. Figure 4a).

3.4. Effect of Surface Modification on Water Permeance.

Figure 5 shows the effect of dopamine coating time at 2 g/L dopamine on the relative water permeance (which is defined as the ratio of water permeance in the modified membrane to that in the uncoated one). Error bars are standard deviations of measurements from six membrane samples. The water permeance decreases significantly as the coating time increases from 0 to 5 h. For example, the reduction is 36% after 1-h coating and 92% after 5-h coating in the PDA coated PES-2. For PSf-100, the water permeance levels off after 5-h coating. This trend is in good agreement with the thickness of the PDA layer on PSf films. As shown in Figure 2b, the PDA layer thickness increases and then levels off after 5-h coating. A thicker coating layer decreases porosity and pore size of the membrane surface, though the hydrophilicity of the membrane surface increases.[16,34,73,74] Additionally, increasing the dopamine concentration in the coating solution decreases the water permeance, as shown in Figure S2 in the Supporting Information.

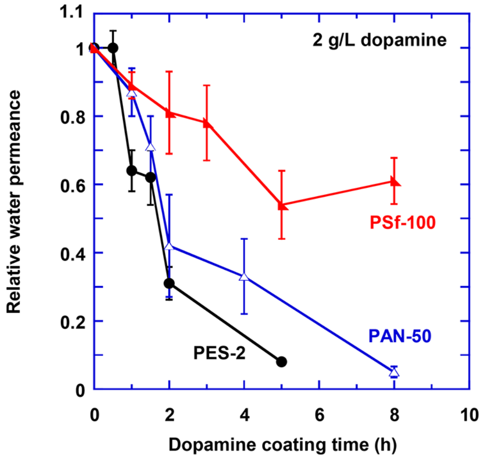


Figure 5. Effect of dopamine coating time on the relative water permeance in PES-2, PAN-50, and PSf-100 modified with a 2 g/L dopamine solution. The water permeance was determined at a transmembrane pressure difference of 30 psi. The curves are to guide the eye.

Figure 5 also shows that the permeance values decrease with increasing the coating time follows the order PSf-100 < PAN-50 < PES-2. For example, after 5-h coating, the water permeance decreases by 48%, 70%, and 92% for PSf-100, PAN-50, and PES-2, respectively. This trend is consistent with that of the pore size in these membranes, as indicated by the MWCO of 100 kDa, 75 kDa, and 4 kDa for PSf-100, PAN-50, and PES-2, respectively. With the similar coating layer thickness, membranes with smaller pore size (or MWCO) would have more substantial decrease in the relative pore size and thus relative water permeance.

Figure 6a shows the effect of SBMA content in the coating solution on the water permeance of the modified membranes. In contrast to the PDA modification using 2 g/L dopamine, the SBMA/PDA modifications were performed with coating solutions containing 1 g/L dopamine to obtain high water permeance (as shown in Figure S2 in the Supporting Information).

The PDA coating decreases the water permeance. On the other hand, the introduction of SBMA in the coating solution with dopamine increases the water permeance. For example, as the SBMA content increases from 1 g/L to 4 g/L, the relative water flux in the coated PSf-100 increases from 0.74 ± 0.08 to 0.92 ± 0.01. This behavior can be ascribed to the improved hydrophilicity (cf. Figure 4b) and the constant thickness of the coating layer with increasing SBMA content. As shown in Figure 2a, increasing SBMA content in the coating solution has a negligible effect on the coating layer thickness and presumably pore size and porosity. On the other hand, increasing the hydrophilicity increases the wettability and thus the accessibility of small pores, which would be too hydrophobic for water transport otherwise.[4,63]

Figure 6b presents the effect of coating time on the relative water permeance in the membranes coated using a solution containing 1 g/L dopamine and 4 g/L SBMA. The relative water permeance decreases initially with increasing coating time and then levels off, which can be ascribed to the change in the thickness and hydrophilicity of the coating layers. As shown in Figure 2b, the coating layer thickness increases initially with increasing the SBMA/PDA codeposition time and then levels off. The surface hydrophilicity does not further improve after 2-h coating (cf. Figure 4c). The modified PSf-100 with SBMA/PDA exhibits only 4% reduction after 8-h coating, because PSf-100 has a larger pore size than PES-2 and PAN-50 and the reduction in pore size and porosity in PSf-100 has less adverse effect on the water permeance than that in the other two membranes.

3.5. Effect of Surface Modification on Antifouling Properties.

To evaluate the effect of surface modification on the water permeance in the presence of foulants, the membranes were tested with model wastewater containing BSA under crossflow mode. The conditions of surface modification were chosen to achieve the balanced hydrophilicity (as shown in Figure 4) and water permeance (as shown in Figures 5 and 6) for all three membranes. Specifically, the coating time is 1, 1.5, and 2 h for PES-2, PAN-50, and PSf-100, respectively. The PDA modification used 2 g/L dopamine solution, and the SBMA/PDA modification used a solution containing 1 g/L dopamine and 1 g/L SBMA for PES-2 and a solution containing 1 g/L dopamine and 4 g/L SBMA for PAN-50 and PSf-100.

Figure 7 exhibits the water permeance as a function of time during filtration of water containing 3 g/L BSA. The detailed

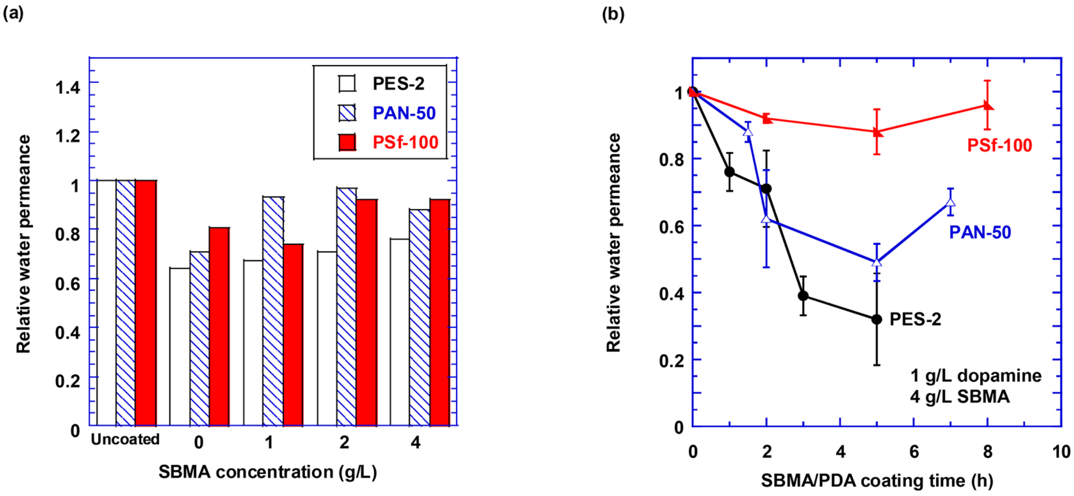


Figure 6. Relative water permeance at a transmembrane pressure of 30 psi as a function of (a) SBMA content in the coating solution containing 1 g/L dopamine and (b) SBMA/PDA coating time using 1 g/L dopamine and 4 g/L SBMA. For (a), the PDA only coating was achieved with 2 g/L dopamine, and the coating time is 1, 1.5, and 2 h for PES-2, PAN-50, and PSf-100, respectively.

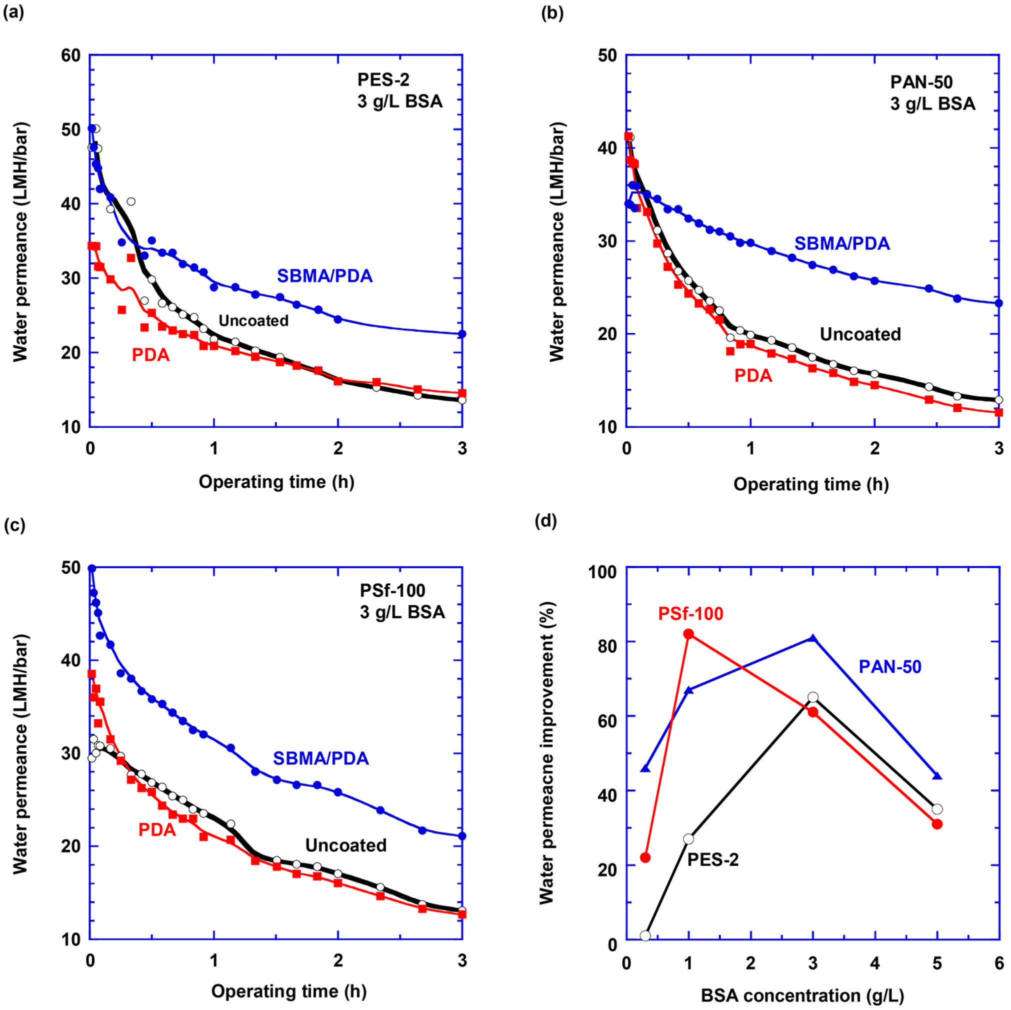


Figure 7. Water permeance as a function of filtration time in unmodified, PDA modified, and SBMA/PDA coated samples for (a) PES-2, (b) PAN-50, and (c) PSf-100 tested in a crossflow system using a 3 g/L BSA solution. (d) Effect of the BSA content in the model wastewater on the water permeance improvement (after 3-h filtration).

results with BSA concentrations of 0.3, 1, and 5 g/L are presented in Figure S3 in the Supporting Information. In general, water permeance decreases with time due to the fouling of the membranes by BSA. For all membranes, the PDA modified membranes exhibit water permeance similar to that of the corresponding unmodified ones after long-term operation,

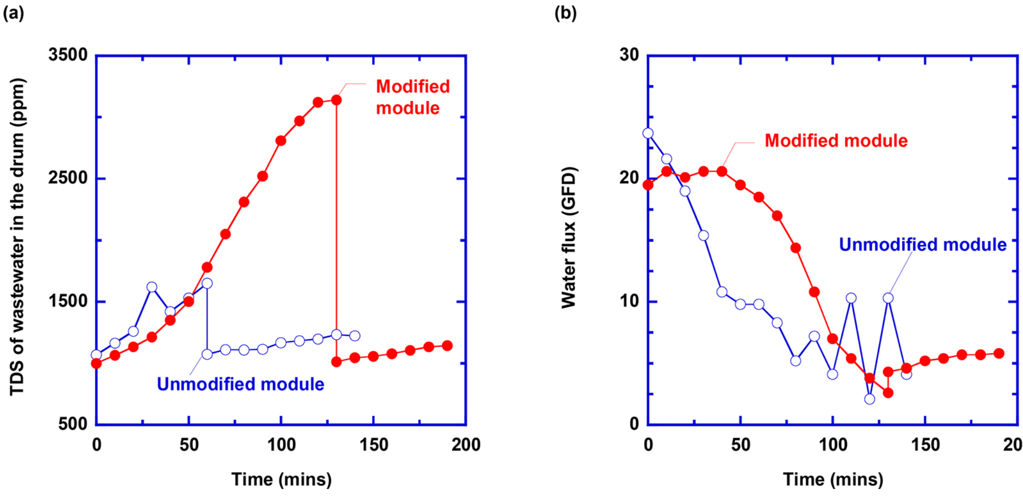


Figure 8. Field testing results of an unmodified and a modified module in a batch operation at a wastewater treatment plant. (a) The salt content in the feedwater as a function of operation time during runs. Fresh wastewater was added at 60 min for the unmodified module and at 130 min for the modified one. (b) Water flux in the surface-modified membrane module and the unmodified one as a function of operation time.

indicating that the PDA layer does not have sufficient antifouling properties to provide high water permeance in the long term, despite the improved surface hydrophilicity. The coating with SBMA/PDA increases the long-term water permeance compared with the unmodified membranes, due to the enhanced antifouling properties on the modified membrane surface.

Figure 7d clearly illustrates the benefit of zwitterion coating, as indicated by the long-term water permeance improvement (defined as the percentage of the water permeance increase in the modified membrane relative to the unmodified one after 3-h operation in this study). Increasing the BSA content significantly increases the permeance enhancement before decreasing, which can be explained below. As the BSA content increases, the fouling becomes more significant for unmodified membranes, and thus the long-term permeance decreases with increasing BSA content. On the other hand, the increased antifouling properties derived from the SBMA/PDA coating demonstrate the great benefits, and thus the permeance enhancement increases with increasing the BSA content. However, as the BSA content further increases to 5 g/L, the membranes are significantly fouled due to the BSA adsorption, even for those with the SBMA/PDA modification. Therefore, the permeance enhancement decreases. Nevertheless, the SBMA/PDA modification shows positive improvement of water permeance, demonstrating the effectiveness of the grafted zwitterions on the membrane surface to improve the antifouling properties.

There are a variety of methods for membrane surface modification aiming to improve antifouling properties and thus long-term water permeance.[3] Considering vastly different membranes and foulants evaluated, it is beyond the scope of this study to perform a thorough comparison. Instead, an exampled comparison is made with UF membranes modified with PDA and methyl-terminated poly(ethylene glycol) amine (m-PEG-NH_2/PDA) in a two-step surface modification. Compared with the unmodified ones, the m-PEG-NH_2/PDA modified PSf and PES membranes exhibited an enhanced water permeance by 145% and 35%, respectively, after 1-h filtration of oily water in a constant pressure crossflow system.[4] On the other hand, the m-PEG-NH_2/PDA modified PSf membranes did not exhibit improvement when challenged in continuous biofouling experiments with foulants such as BSA.[24] To put this into perspective, the SBMA/PDA coating on PES membranes in this study increases the water flux by as high as 65% when tested with 3 g/L BSA solution, compared with the uncoated one, as shown in Figure 7d. This result demonstrates the effectiveness of the surface modification by SBMA/PDA developed in this study.

3.6. Modification of a Commercial NF Membrane Module and Its Field Tests. To further demonstrate the versatility of our approach, we have modified a commercial NF membrane module using a solution containing 2 g/L dopamine and 8 g/L SBMA. This module was tested in a batch mode with a feed pressure of 150 psig and a drum containing real wastewater from a wastewater treatment plant. The permeated water was released, and the rejected water was recycled back to the drum. During the treatment, the content of the contaminants such as total dissolved salts (TDS) and organic matter increased with time, as shown in Figure 8a. Fresh wastewater was also added to the drum before the water level became too low in the drum. For the modified module, the feed contained higher salts than that for the unmodified one, due to the higher water flux through the modified one.

Figure 8b directly compares the water flux in the modified module with the unmodified one. The modified module demonstrates higher water flux for most of the first 100 min than the unmodified one. These results are consistent with those obtained for membranes challenged with the BSA solutions, suggesting that the BSA can be a model foulant for the study of antifouling properties. After 100 min, both modules show comparable water flux, though the feed salt content is much higher for the modified module. For a typical operation, the membrane modules may be cleaned within 2 h, and thus, the modified modules would process much more water than the unmodified one.

The fouling in the modified module is also reversible, suggesting its promising antifouling properties. For example, after two runs of the fouling test, the modified module exhibited water flux of 5.7 GFD (gallon per square foot per day). The module was then cleaned using tap water, and the water flux increased to 16 GFD, which was about 82% of the flux in the unused module.

The stability of the SBMA/PDA coating on the membranes underwater was also investigated. After the surface coating with SBMA/PDA, the module was kept in water for about one month before the field test. The superior performance over the unmodified one indicates the robustness of the surface coating underwater. More importantly, the modified module showed stable separation performance after 4 cycles of operation (with wastewater and then tap water) in the field. However, the membrane modules were not subjected to cleaning with chemicals in this study. Nevertheless, PDA coated membranes have demonstrated long-term stability in operation or with chemical cleaning. For example, a PSBMA/PDA coated MF membrane showed stable water flux after continuously being exposed to hot water at 60 °C for 27 days;[63] the PDA-coated NF membranes showed much more stable performance than the unmodified one after exposure to a solution containing 50 ppm sodium hypochlorite (NaClO).[75] More importantly, membrane modules modified with PEG/PDA have demonstrated stability with cleaning using a heated caustic cleaning solution and citric acid in the field test with produced water.[25]

4. CONCLUSIONS

We have demonstrated a facile approach to graft zwitterions on the membrane surface via codeposition of dopamine and zwitterions with methacrylate groups. The dopamine acts as a bioglue, while the amine groups react with methacrylates to covalently graft the zwitterions onto the membrane surface. The versatility of this approach has been successfully demonstrated for three UF membranes with various chemistries and pore sizes. The surface modification increases surface hydrophilicity and leads to enhanced long-term water permeance when tested with water containing BSA as a model biofoulant. The simplicity and yet effectiveness of this approach have also been demonstrated for postmodification of a commercial NF membrane module, which shows improved water permeance when treating real wastewater at a wastewater treatment plant.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b02378.

> ATR-FTIR results for the surface modified membranes; XPS results for the surface modified membranes; effect of dopamine content in the coating solutions on water permeance; and effect of surface modification on long-term water permeance (PDF)

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Notes

Any opinions, findings, and/or interpretations of data contained herein are the responsibility of the authors and do not necessarily represent the opinions, interpretations, or policy of Rochester Institute of Technology and its NYS Pollution Prevention Institute or the State.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of this work by New York State Pollution Prevention Institute R&D Program provided by the Environmental Protection Fund as administered by the New York State Department of Environmental Conservation. We are also thankful for the partial support from the U.S. National Science Foundation Division of Civil, Mechanical and Manufacturing Innovation (CMMI) with a grant number of 1635026. We also are thankful for the advice on the membrane surface modification using dopamine from Professor Benny Freeman at the University of Texas at Austin.

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