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Does Hydrophilic Polydopamine Coating Enhance Membrane Rejection of Hydrophobic Endocrine-Disrupting Compounds?

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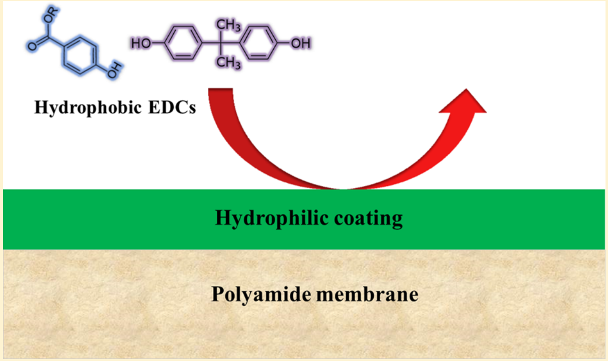
Ⓢ *Supporting Information*

ABSTRACT: Endocrine-disrupting compounds (EDCs), an important class of micropollutants with potent adverse health effects, are generally poorly rejected by traditional thin film composite polyamide membranes and thus pose significant risks in membrane-based water reclamation. We hypothesize that membrane rejection of hydrophobic EDCs can be enhanced by a hydrophilic surface coating. Using polydoamine (PDA) as a model hydrophilic coating layer, the PDA-coated NF90 membrane experienced an up to 75% reduction in the passage of bisphenol A compared to the control (NF90 without coating). Meanwhile, we also observed a systematic increase in the level of rejection of three hydrophobic parabens with an increase in PDA coating time. In contrast, there were no systematic changes in the rejection of neutral hydrophilic polyethylene glycol, which suggests that the enhanced rejection of EDCs was due to weakened EDC−membrane hydrophobic interaction. Further sorption tests revealed that the hydrophilic PDA coating could effectively decrease the rate of sorption of EDCs by the membrane, which is responsible for the improved rejection as predicted by the solution−diffusion theory. This study reveals an exciting opportunity for engineering membrane surface properties to enhance the rejection of targeted micropollutants, which has important implications in membrane-based water reclamation.



■ INTRODUCTION

The grand challenge of water scarcity calls for more sustainable water resource management.[1,2] Reclamation from municipal wastewater, e.g., using membrane-based reverse osmosis (RO) and nanofiltration (NF), can play an important role in addressing this challenge because of its practically unlimited supply.[1,3−8] RO and NF membranes reject a variety of contaminants, including dissolved ions.[9] Nevertheless, some organic micropollutants with low molecular weights, neutral charges, and/or high hydrophobicities can still pass through RO/NF membranes.[10−13] One important class of micropollutants consists of endocrine-disrupting compounds (EDCs). Because of their ubiquitous occurrence in municipal wastewater[14−16] and potent endocrine disrupting effects even at trace concentrations,[17] the presence of EDCs in reclaimed water has been regarded as one of the most critical risks associated with water reclamation.[18]

The existing literature on RO/NF membrane preparation centers on the optimization of water permeability and salt rejection as well as antifouling performance.[19,20] Generally, a modern RO/NF membrane based on polyamide chemistry can easily achieve high salt rejection (e.g., ≥99% for NaCl by RO and ≥90% for divalent ions by NF).[21,22] However, some studies have reported insufficient rejection (e.g., ≲50%) of those membranes for neutral and hydrophobic EDCs, and the low rate of rejection was often attributed to the hydrophobic interaction between the compounds and membrane surface.[12,23−25] Indeed, many studies have consistently reported that more hydrophobic compounds tend to have lower rates of rejection under otherwise similar conditions (e.g., comparable molecular size), citing their increased level of sorption by RO/NF membranes as a main cause.[10,12,23−28] On the other hand, fewer studies have systematically investigated the role of membrane surface hydrophilicity/hydrophobicity in the rejection of trace organic compounds such as EDCs. We therefore hypothesize that the rejection of hydrophobic EDCs can be significantly enhanced by improving membrane surface hydrophilicity. If this hypothesis were true, it would open a new dimension for improving membrane rejection of EDCs, e.g., by membrane surface coating or grafting.

In this study, we prepared a hydrophilic surface coating on a commercial nanofiltration membrane and systematically investigated its effect on the removal of four hydrophobic

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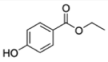
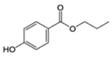
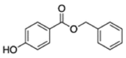
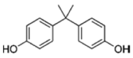
Table 1. Physicochemical Properties of the Four EDCs

Compound	Formula	Structure	MW	pKa	log K_{ow}
Ethylparaben	$C_9H_{10}O_3$		166.2	8.31[a]	2.4[b]
Propylparaben	$C_{10}H_{12}O_3$		180.2	8.23[a]	2.9[b]
Benzylparaben	$C_{14}H_{12}O_3$		228.2	8.18[a]	3.6[b]
BPA	$C_{15}H_{16}O_2$		228.3	10.2[c]	3.3[c]

[a] Data obtained from ref 35. [b] Data obtained from ref 36. [c] Data obtained from ref 37.

Table 2. Membrane Surface Properties and Separation Performance of Uncoated and PDA-Coated NF90

membrane	water permeability (L m^{-2} h^{-1} bar^{-1})[a]	NaCl rejection (%)[a]	water contact angle (deg)[b]	surface energy (mN/m) total	surface energy (mN/m) polar	surface energy (mN/m) dispersive	roughness R_a (nm)	PEG rejection (%)[c]
NF90	7.06 ± 0.69	83.5 ± 2.9	69.8 ± 1.8	37.4	13.6	23.8	50.8 ± 11.8	86.0 ± 1.8
NF90-C0.5	6.70 ± 0.89	84.8 ± 1.4	66.3 ± 1.2	40.8	19.9	20.9	57.8 ± 9.0	85.2 ± 4.3
NF90-C1	5.80 ± 0.86	82.7 ± 1.4	58.3 ± 2.6	42.0	19.9	22.1	61.2 ± 4.7	83.6 ± 4.1
NF90-C2	5.10 ± 0.36	83.1 ± 1.4	61.0 ± 1.9	40.8	18.3	22.5	60.9 ± 12.2	87.8 ± 3.1
NF90-C4	3.91 ± 0.21	86.4 ± 1.1	62.0 ± 2.4	39.8	18.1	21.7	57.2 ± 2.8	81.7 ± 3.0

[a] Experimental condition: 10 mM NaCl, pH 6.6, and 25 °C. The stabilized water flux was determined by weighing permeate water using a digital balance, and salt rejection was determined on the basis of the measured conductivity values of the feed and permeate water (Ultrameter II, Myron L, Carlsbad, CA). The results were calculated from at least three parallel experiments. [b] Contact angle values have been corrected for the roughness effect using the Wenzel equation (see Supporting Information section S2). [c] Experimental condition: 200 ppm PEG 200, 10 mM NaCl, pH 6.6, and 25 °C. PEG samples from bulk solution and permeate were analyzed with a total organic carbon (TOC) analyzer (Aurora 1030, OI Analytical, College Station, TX). The results were calculated from at least three parallel experiments.

EDCs. Polydopamine (PDA), widely studied for membrane antifouling modifications,[29] was adopted as a model coating material because of its easy preparation and its ability to form stable films on a wide range of substrates.[30−34] Our results have important implications for membrane design tailored for water reclamation based on the nature of targeted organic micropollutants.

■ MATERIALS AND METHODS

General Chemicals. Unless described otherwise, all solutions were prepared from analytical-grade chemicals and deionized (DI) water. Dopamine hydrochloride (J&K Scientific Ltd.) and tris (Acros Organics, Geel, Belgium) were used for membrane surface coating. Polyethylene glycol [PEG, average molecular weight (MW) of ∼200 (Aladdin)] was used to evaluate membrane rejection of the hydrophilic neutral compound. Sodium chloride (Uni-Chem), hydrochloride acid (37 wt %, VWR, Dorset, U.K.), and sodium hydroxide (Uni-Chem) were used for solution chemistry adjustment. Optima-grade methanol (Fisher Scientific, Pittsburgh, PA) was used for ultraperformance liquid chromatography coupled with tandem mass spectrometry (UPLC−MS/MS) analysis and for EDC extraction.

EDCs. Four EDCs were investigated in this study, including ethylparaben (99%), propylparaben (99%), benzylparaben (≥99%), and bisphenol A (BPA, 97%). BPA was obtained from Acros Organics, and the other EDCs were supplied by Sigma-Aldrich (St. Louis, MO). The physicochemical properties of the EDCs are summarized in Table 1. A stock solution of each EDC (1 g/L) was prepared by dissolving the compound into methanol and stored at −20 °C.

Membrane. A commercial nanofiltration membrane, NF90, was provided by Dow Chemical Co. NF90 is a thin film composite (TFC) membrane, with a fully aromatic polyamide as its rejection layer.[38] The membrane was thoroughly rinsed with DI water to remove any impurities and was soaked in DI water for at least 24 h before further use.

Preparation of the PDA Coating. A hydrophilic PDA coating was prepared by the self-polymerization of dopamine at room temperature (∼25 °C) following the procedures described by Lee et al.[30] Briefly, a pristine membrane coupon was placed in a custom-designed container (Supporting Information section S1) with only its rejection layer exposed for coating. A 300 mL dopamine hydrochloride/tris solution [0.2 wt % dopamine hydrochloride, 10 mM tris solution (pH 8.5)] was added to the container, and the self-polymerization was performed under moderate shaking for a predetermined duration (0.5, 1, 2, and 4 h). Coated membranes are denoted as NF90-C0.5, NF90-C1, NF90-C2, and NF90-C4, respectively, in accordance with their coating time. The coated membranes were thoroughly rinsed with DI water to remove any unreacted residues. According to the published literature, the PDA coating is very stable (e.g., under ultrasonic treatment[39] or over long time exposure[40]).

Membrane Characterization. Membrane surface morphology was characterized by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). Vacuum-dried membrane samples were sputter-coated with a thin layer of gold (BAL-TEC SCD 005), and SEM micrographs were obtained at an acceleration voltage of 5 kV. Atomic force microscopy (AFM) was employed to determine the membrane surface roughness using a scanning probe microscope (Dimension 3100, Veeco, Plainview, NY) with a scan area of 10 μm × 10

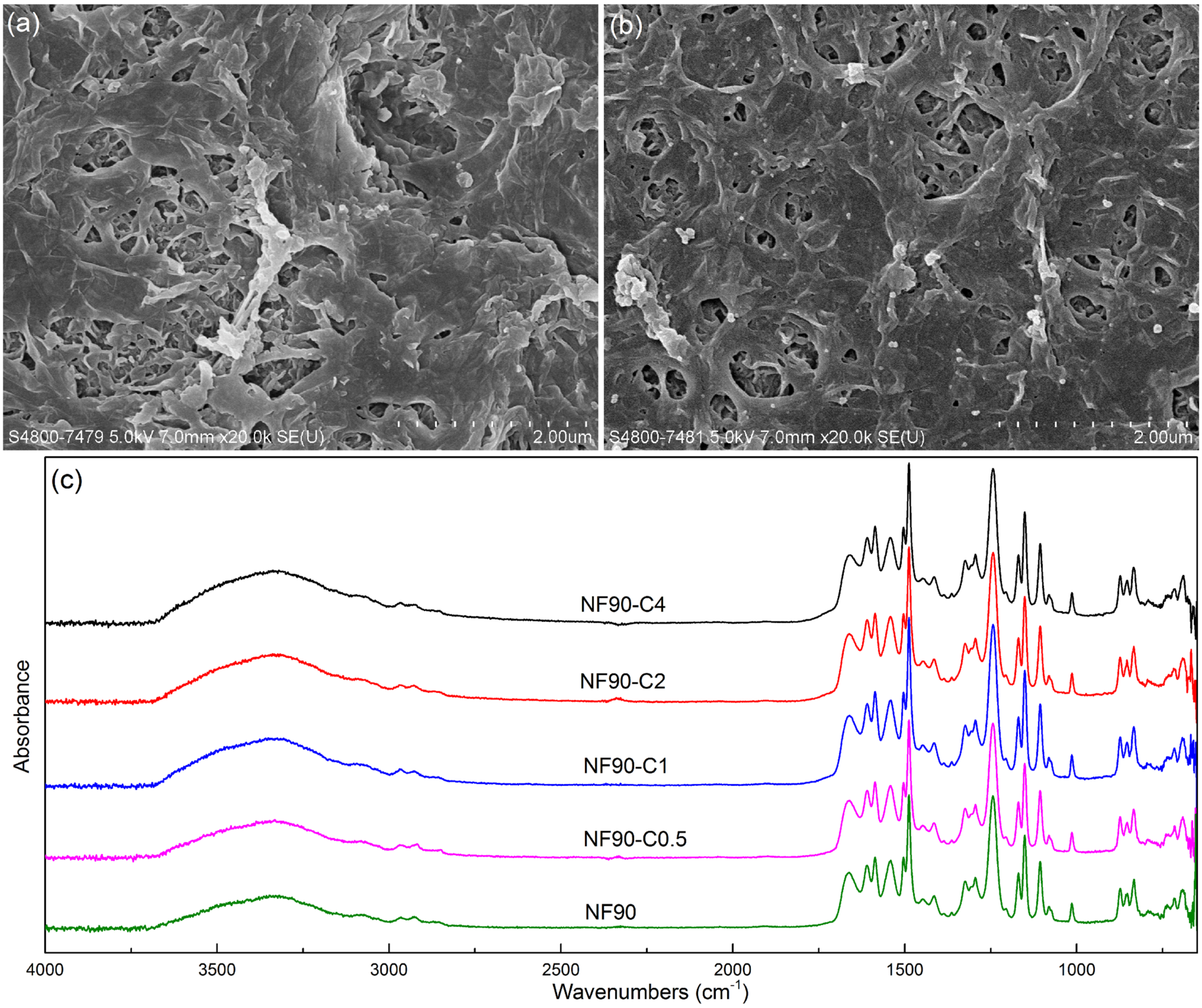


Figure 1. SEM images of the active layer of (a) original NF90 and (b) NF90-C1. (c) ATR-FTIR spectrum of active layers of NF90-C4, NF90-C2, NF90-C1, NF90-C0.5, and NF90.

μm. Average roughness R_a was determined by Nanoscope software (Bruker, Camarillo, CA). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was conducted with a Nicolet 6700 FTIR spectroscope (Thermo Fisher Scientific, Waltham, MA) over a wavenumber range from 650 to 4000 cm^{-1}. Contact angle tests were conducted by using a contact angle goniometer (OCA20, Dataphysics) at 25 °C. Three probing liquids, including water (H_2O; surface tension γ = 72.80 mN/m), diiodomethane (CH_2I_2; γ = 50.80 mN/m), and glycerol ($C_3H_8O_3$; γ = 63.30 mN/m), were used to obtain surface energy [calculated by SCA software from Dataphysics using the Owens−Wendt−Kaelble approach[41,42] (see Supporting Information section S2)]. The reported results roughness, contact angle, and surface energy are the average values of at least five parallel measurements. X-ray photoelectron spectroscopy (XPS) was performed using an SKL-12 spectrometer (Leybold, Sengyang, China) equipped with a VG CLAM 4 MCD electron energy analyzer. The X-ray source was an Al Kα gun (1496.3 eV) operated at 10 kV and 15 mA. A spectral range of 0−1000 eV were scanned at a scanning resolution of 0.1 eV.

EDCs Rejection Tests. A laboratory-scale cross-flow membrane filtration setup was used to evaluate the rejection of EDCs [Supporting Information section S3 (Laboratory cross-flow filtration setup)]. To allow membrane precompaction, a 10 L feed solution containing 10 mM NaCl (pH 6.6, 25 °C) was recirculated for 12 h at 10 bar with a cross-flow velocity of 22.4 cm/s. Membrane permeability and rejection were measured at an applied pressure of 8 bar (see the footnotes of Table 2). Stock solutions of EDCs were then introduced into the feed tanks to achieve a concentration of 200 μg/L for each EDC compound. Filtration experiments were continued for an additional 12 h before the collection of feed and permeate samples for EDC analysis. To determine the amount of EDCs absorbed by the membranes, the EDC-filtered membrane samples were gently rinsed with DI water and placed into a 100 mL 50% methanol solution for extraction of EDCs for 24 h at room temperature.[23] All the experiments were performed in triplicate.

Analytical Method for EDCs. EDC analysis was performed by UPLC−MS/MS via an optimized method. Chromatographic separation of EDCs was achieved within 1.5 min by linear gradient conditions using a 50 mm × 2.1 mm

BEH C18 column (particle size of 1.7 μm). Tandem quadrupole mass spectrometers (Waters, Milford, MA) were equipped to conduct the MS/MS scan. Other optimized parameters are described in detail in Supporting Information section S4 (UPLC-MS/MS operational condition).

RESULTS AND DISCUSSION

Membrane Characterization. Panels a and b of Figure 1 show SEM images of the original membrane NF90 and the coated membrane NF90-C1, respectively. NF90-C1 had an appearance similar to that of NF90: both membranes presented the ridge-and-valley roughness structure that is characteristic of polyamide membranes,[43] although some fine features in the valley regions of NF90-C1 appeared to be covered. In addition, the PDA coating did not significantly change the membrane surface roughness (Table 2). These results suggest that the coating thickness was much thinner than the membrane surface roughness (∼60 nm). According to a prior study,[30] the PDA thickness was estimated to grow at a rate of 5 nm/h and reached ∼20 nm after being coated for 4 h.

ATR-FTIR spectra (Figure 1c) show no apparent changes between the original NF90 and the PDA-coated membranes over the wavenumber range of 650−2000 cm^{-1}, due to overlapping characteristic peaks of PDA and polyamide.[44] However, the broad peak centered around 3300 cm^{-1} became more intense upon PDA coating because of the presence of catechol OH groups in PDA.[45] It is also worth noting that ATR-FTIR has a shallower sample penetration depth at higher wavenumbers (≲200 nm at >3300 cm^{-1}), making this region of the spectra more sensitive to surface coatings.[46] XPS results showed a reduction in N content (8.94% for NF90 and 7.08% for NF90-C4) and an increase in O content (15.7% for NF90 and 18.6% for NF90-C4) after coating had been performed for 4 h, which is consistent with the presence of PDA.

PDA coating decreased the water contact angle of the membrane from 69.8° (NF90) to 66.3° for NF90-C0.5 and ∼60° for NF90-C1 to NF90-C4 (Table 2). Surface energy analysis indicates that PDA coating increased the total surface energy, which was largely due to the increase in the polar components. These results confirm that the coated membranes became more hydrophilic.

EDC Rejection and Sorption Tests. Figure 2a shows the rejection of the four EDCs by the original membrane NF90 (the control) and the PDA-coated membranes. PDA-coated membranes consistently had enhanced rejection (and lower passage) compared with that of the control. The rates of rejection of ethylparaben, propylparaben, and benzylparaben increased from ∼50, ∼50, and ∼35% for NF90 to ∼70, ∼70, and ∼60% for NF90-C4, respectively. BPA showed a relatively high rate of rejection of ∼96% for the control. Though the rates of rejection of the coated membranes were only slightly increased (e.g., ∼99% for NF90-C4), the corresponding transmission was dramatically reduced by $^{3}/_{4}$ (Figure S4), leading to a greatly improved permeate quality. The enhancement effect was more obvious at longer coating times, which can be attributed to a thicker PDA layer[30] and thus a greater resistance to solute transport because of a longer diffusion path according to the solution−diffusion theory.[9] The improved rejection of EDCs can be attributed to the weakened hydrophobic interaction due to the inclusion of the hydrophilic coating. On the other hand, size exclusion and charge repulsion were unlikely responsible for the enhancement effects based on the following observations (Table 2). (1) The PDA coating did not obviously enhance the rejection of PEG, a neutral hydrophilic compound that is commonly used to characterize membrane pore size and thus to assess the effect of size exclusion. (2) No systematic changes were observed for the rejection of a NaCl electrolyte solution upon PDA coating.

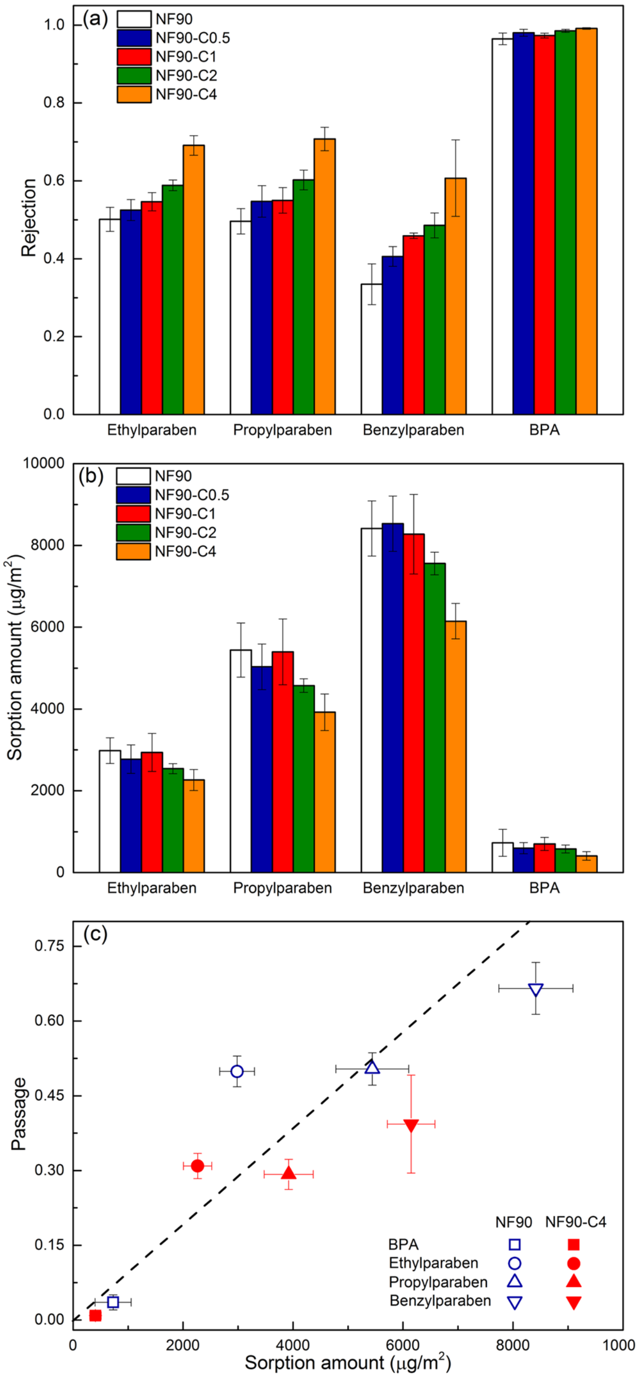


Figure 2. (a) Rejection of EDCs by original NF90 and PDA-coated NF90. (b) Sorption of EDCs on original NF90 and PDA-coated NF90. (c) Plot of the amount of sorption of EDCs on the membrane and passage through the membrane based on the data of NF90 and NF90-C4 (r^2 = 0.761).

To improve our understanding of the role of EDC−membrane hydrophobic interaction in their rejection behavior, sorption experiments were performed for the four EDCs on both uncoated and coated membranes (Figure 2b). All the compounds showed a reduced rate of sorption upon PDA

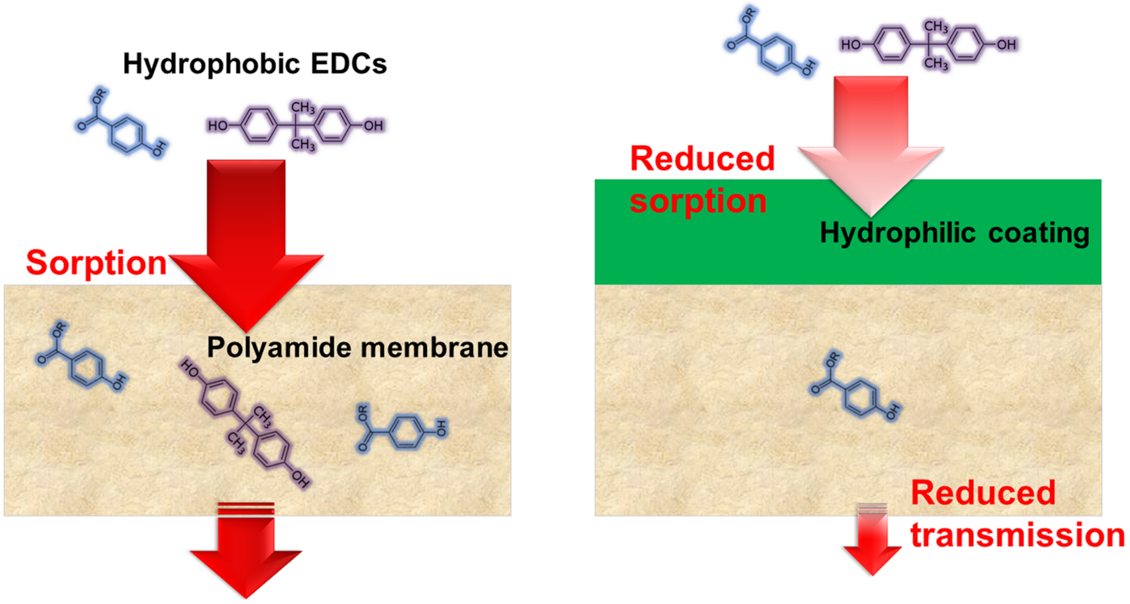


Figure 3. Conceptual diagram of the sorption and transmission of hydrophobic EDCs through original and coated membranes.

coating, as a result of the hydrophilic nature of PDA. Figure 2c shows a clear correlation between the sorption of EDCs and their passage through the membranes: a high rate of sorption was associated with a high rate of passage of EDCs (thus a low rate of rejection). Compared to NF90, the coated membrane NF90-C4 simultaneously had a greatly reduced rate of sorption and a lower rate of passage (Figure 3). On the basis of the solution−diffusion theory,[47] the transport of solute through a dense membrane is governed by the sorption of the compound by the membrane and its diffusion through the membrane matrix.[12] Both enhanced sorption and enhanced diffusion can lead to greater solute transmission. The strong correlation between sorption and passage in this study implied the dominant role of the reduced rate of sorption in promoting a higher rate of rejection, providing strong evidence for our hypothesis of the beneficial effect of the hydrophilic PDA coating.

IMPLICATIONS

The existing literature about RO/NF membrane synthesis focuses on the optimization for water permeability, salt rejection, and antifouling performance. The rejection of organic micropollutants is not explicitly used as a target for optimization, despite their environmental and health significance being far more important than that of simple inorganic salts such as NaCl in the context of water reclamation. On the other hand, many studies revealed that membranes with a high rate of NaCl rejection do not necessarily have adequate rejection of many organic micropollutants.[10−13] This study bridges the gap between membrane synthesis and its applications for water reclamation and demonstrates the feasibility of engineering membrane surface properties to enhance the rejection of the target contaminants.

Using a hydrophilic PDA coating, the rates of both the sorption and transmission of EDCs through a nanofiltration membrane were significantly reduced by avoiding unfavorable hydrophobic interaction between the compounds and the membrane surface. In the existing membrane literature, PDA has been widely studied as a surface coating material to impart antifouling properties to membranes.[29] Combined with the findings in this study, PDA shows good potential for water reclamation applications with simultaneous improved rejection of trace contaminants and membrane flux stability. Our study may open a new paradigm for improving the rejection of organic micropollutants in water reclamation by tailoring membrane architecture/chemistry on the basis of the nature of targeted organic compounds. A well-designed membrane can potentially address not only membrane fouling but also product water quality, bringing the benefits of long-term operational stability and minimized health risks associated with water reclamation.

One important concern for the PDA coating approach is the potential loss of membrane permeability. Thus, future studies shall explore additional surface modification methods (e.g., grafting of hydrophilic or zwitterionic polymers[48]) for enhancing the rejection of trace organic contaminants without sacrificing water permeability. In addition, despite the common adoption of polyamide membranes for water reclamation, the development of non-polyamide-based hydrophilic membranes with tailored EDC rejection performance can be promising.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00263.

> Preparation of PDA-coated membranes (section S1), procedures for surface energy determination (section S2), laboratory cross-flow filtration setup (section S3), UPLC−MS/MS operational conditions (section S4), effect of PDA coating on the passage of BPA (section S5), and effect of filtration time on the rejection of EDCs (section S6), and extraction of EDCs (section S7) (PDF)

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Y.D. and Z.T. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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