

A THIN FILM NANOFILTRATION MEMBRANE

BACKGROUND

Nanofiltration, a pressure-driven membrane separation process, has become an important separation and purification technique in water treatment, pharmaceutical purification, and petrochemical separation.

Conventional nanofiltration membranes are flat sheets containing a thick support layer, which provides sufficient mechanical strength to withstand high pressure in a nanofiltration application. On the other hand, the thick layer has great transport resistance and thus hinders solvent permeation. See Petersen, Journal of Membrane Science, 83, 81–150 (1993).

Hollow fiber membranes are usually made from dopes of much higher concentrations than those used for preparing flat sheet membranes so as to maintain self-supported mechanical strength. As a result, hollow fiber membranes have smaller pores. They thus provide a solvent permeability even lower than that of flat sheet membranes. See Baker, Membrane Technology and Applications (John Wiley & Sons Ltd., 2004); and Wang et al., Journal of Membrane Science, 281, 307–15 (2006).

Further, conventional nanofiltration membranes have a low solute rejection for ions and compounds having low molecular weights.

There is a need to develop a nanofiltration membrane that has both a high solvent permeability and a high solute rejection.

SUMMARY

This invention is based on an unexpected discovery of a thin film polymeric membrane for nanofiltration that has a low molecular weight cut off, a high pure water permeability, and a high rejection for charged molecules.

One aspect of this invention relates to a polymeric membrane containing a macrovoid layer, a first porous layer, a second porous layer, and a thin film layer.

The macrovoid layer, including a first side and a second side, has a pore size of 0.001 to 100 μm and a thickness of 20 to 2000 μm . The second porous layer, covering the second side of the macrovoid layer, has a pore size of 0.001 to 100 μm and a thickness of 1 to 20 μm .

Each of the macrovoid layer and the second porous layer can be, independently, made of cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose dibutyrate, cellulose tributyrates, polyacrylonitrile, polyvinyl alcohol, polyamide, polyimide, sulphonated polyimide, polyamide-imide, sulphonated polyethersulphone, sulphonated polysulphone, polybenzimidazole, polyvinylidene difluoride, polyethersulphone, polysulphone, polytetrafluoroethylene, polyether ether ketone, sulphonated polyether ether ketone, or a combination thereof.

The first porous layer, covering the first side of the macrovoid layer, has a pore size of 0.1 to 200 nm and a thickness of 0.01 to 20 μm . It can be made of polyamide, polyimide, sulphonated polyimide, polyamide-imide, sulphonated polyethersulphone, sulphonated polysulphone, polybenzimidazole, polyethersulphone, polysulphone, cellulose acetate, polyacrylonitrile, polyether ether ketone, sulphonated polyether ether ketone, or a combination thereof.

The thin film layer, covering the first porous layer, has a pore size of 0.1 to 10 nm and a thickness of 0.001 to 2 μm . It can be made of polyamide, polyamide-imide, or a combination thereof. In one embodiment, the thin film layer has a positive or negative charge (e.g., a positive charge) and the first porous layer has a charge (e.g., a negative charge) opposite to that of the thin film layer.

The polymeric membrane of this invention, which can be a sheet or a cylinder (e.g., a tube and a hollow fiber), has a molecular weight cut off of 100 to 5000 Dalton and a pure water permeability of 0.1 to 200 $\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$.

Another aspect of this invention relates to a method of rejecting a substance in a liquid. The method includes the steps of (1) providing a mixture of a substance and a liquid, and (2) bringing the mixture in contact with the above-described membrane so as to allow the liquid to pass through the membrane, whereby rejecting the substance on the membrane via size exclusion, Donnan exclusion, or both. The substance has a charge, a molecular weight over 100 Dalton, a particle size over 0.3 nm, or a combination thereof. The liquid is neutral and has a molecular weight below 100 Dalton.

A further aspect of this invention relates to a method of preparing a polymeric membrane. This method includes the steps of (1) providing a support membrane having a first porous layer, a second porous layer, and a macrovoid layer between the

first porous layer and the second porous layer; and (2) coating the support membrane with a thin film layer by interfacial polymerization to obtain a polymeric membrane. The first porous layer, the second porous layer, the macrovoid layer, and the thin film layer are the same as those described above.

- 5 The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and the claims.

DETAILED DESCRIPTION

- 10 Disclosed herein is a polymeric membrane for nanofiltration to reduce water waste or recycle valuable products in many fields, including the textile industry, pharmaceutical industry, and food industry.

The polymeric membrane of this invention can be a flat sheet, a hollow fiber, or of any other desired shape.

- 15 As pointed out above, this membrane contains a macrovoid layer, a first porous layer, a second porous layer, and a thin film layer. The macrovoid layer, the first porous layer, and the second porous layer provide mechanical support to the membrane. The thin film layer, the first porous layer, and the second porous layer, together function as a permeation barrier.

- 20 The macrovoid layer, including a first side and a second side, has a pore size of 0.001 to 100 μm (e.g., 0.01 -1 μm and 0.05-0.1 μm) and a thickness of 20 to 2000 μm (e.g., 50-1000 μm and 80-200 μm). This layer, sandwiched by the first and second porous layers, contains large finger-like macrovoids, providing sufficient mechanical strength against high pressure and having minimal transport resistance for solvent permeation.

25 The first porous layer, covering the first side of the macrovoid layer, has a pore size of 0.1 to 200 nm (e.g., 1-100 nm and 5-20 nm) and a thickness of 0.01 to 20 μm (e.g., 0.1-10 μm and 0.5-5 μm). Preferably, it is negatively charged at pH 1-7 (e.g., pH 2-6 and pH 2-4).

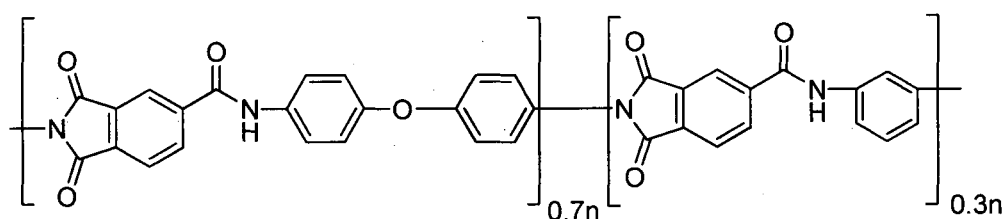
- 30 The second porous layer, covering the second side of the macrovoid layer, has a pore size of 0.001 to 100 μm (e.g., 0.01-1 μm and 0.1-0.5 μm) and a thickness of 1 to 20 μm (e.g., 2-10 μm).

Each of the macrovoid layer, the first porous layer, and the second porous

layer is, independently, made of a polymer that can provide sufficient mechanical support against high pressure. Examples include, but are not limited to, cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose dibutyrate, cellulose tributyrates, polyacrylonitrile, polyvinyl alcohol, polyamide, polyimide, sulphonated polyimide, polyamide-imide, sulphonated polyethersulphone, sulphonated polysulphone, polybenzimidazole, polyvinylidene difluoride, polyethersulphone, polysulphone, polytetrafluoroethylene, polyether ether ketone, sulphonated polyether ether ketone, and a combination thereof.

Preferably, the polymer, which provides support to the membrane, features: (1) superior mechanical properties, allowing nanofiltration at high pressures, (2) good chemical stability over a wide pH range, and (3) charge characteristics introduced by a functional group (e.g., amide, amine, imine, and carboxylic) in its chain. Examples of a chargeable polymer include, but are not limited to, polyamide, polyimide, sulphonated polyimide, polyamide-imide, sulphonated polyethersulphone, sulphonated polysulphone, polybenzimidazole, polyethersulphone, polysulphone, cellulose acetate, polyacrylonitrile, polyether ether ketone, sulphonated polyether ether ketone, and a combination thereof.

Take polyamide-imide as an example. This polymer, which is commercially available (e.g., Torlon[®] 4000T-MV polyamide-imide or Torlon[®] PAI), has the structure of Formula (I) shown below. Note that Torlon[®] PAI membrane support is negatively charged, as demonstrated in Sun et al., AICHE Journal, 56, 1481-94 (2010).



Formula (I)

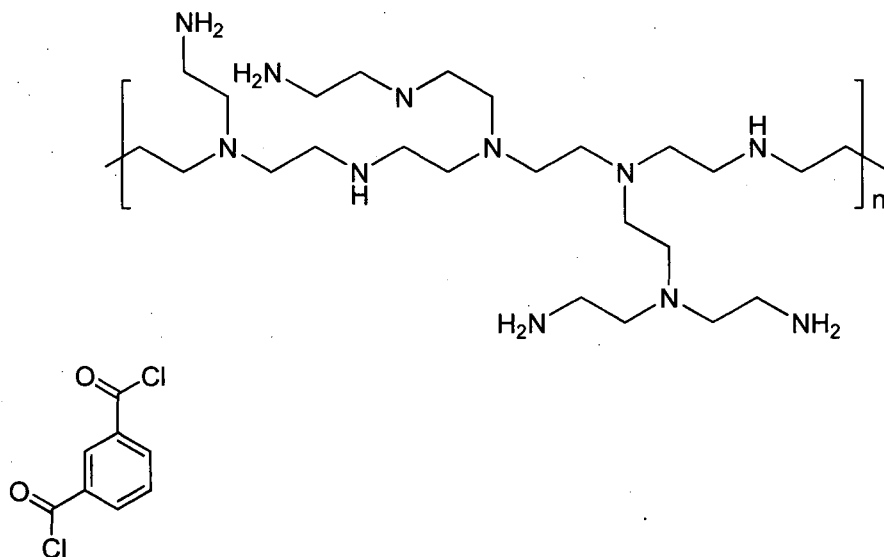
The same polymer, e.g., Torlon[®] PAI, can be used to prepare the macrovoid layer, the first porous layer, and the second porous layer so as to avoid breaking of the membrane support (i.e., a delamination issue). If desired, one can use dope solutions

of the polymer at different concentrations for the three layers separately so as to reduce transport resistance.

Turning to the thin film layer covering the first porous layer, it has a pore size of 0.1 to 10 nm (e.g., 0.2-5 nm and 0.3-1 nm) and a thickness of 0.001 to 2 μm (e.g., 0.01-1 μm and 0.05-0.2 μm). Preferably, the thin film layer is positively charged at pH 6-14 (e.g., pH 7-12 and pH 8-11).

This layer can be made of polyamide, polyamide-imide, or a combination thereof (e.g., hyperbranched polyethylene isophthaloylamide). For examples, it is prepared from interfacial polymerization of two monomers, namely, (1) an amine monomer such as hyperbranched polyethyleneimine, polyepiamine, aliphatic/aromatic polyamine that may contain halo-, silyl- or siloxane-substituents, and a combination thereof, and (2) an acyl halide monomer such as trimesoyl chloride, terephthaloyl chloride, sebacoyl chloride, and a combination thereof.

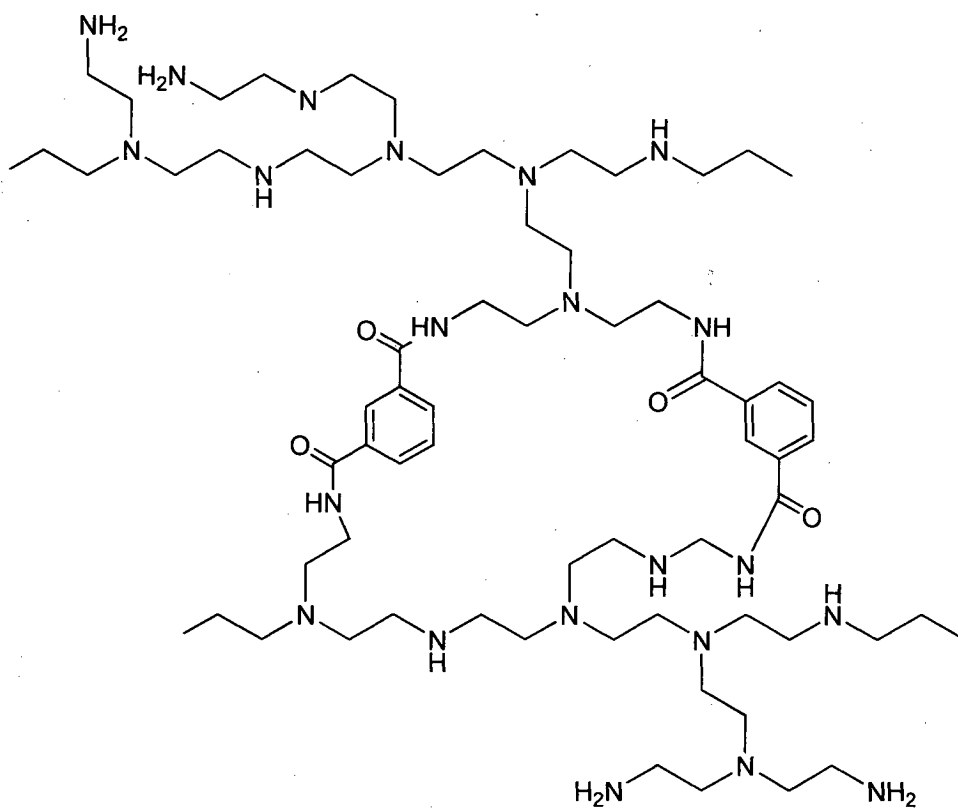
Hyperbranched polyethylene isophthaloylamide, an exemplary polymer of the thin film layer, is formed by an interfacial polymerization of hyperbranched polyethyleneimine (HPEI) and isophthaloyl chloride (IPC), structures of which are shown below as Formulas (II) and (III), respectively. In preparing the thin film layer, the molar ratio of HPEI and IPC can be 0.1 to 10 (e.g., 0.5 to 4 and 1 to 2).



Formula (II)

Formula (III)

Hyperbranched polyethylene isophthaloylamide can have a structure shown below as Formula (IV). It provides a number of amine groups on membrane surfaces. Consequently, the thin film layer can be positively charged below pH 9. As described above, the macrovoid layer, the first porous layer, and the second porous layer, can be negatively charged. Thus, the membrane can be double-repulsive to effectively reject both positively charged molecules and negatively charged molecules, e.g., safranin O ($C_{20}H_{19}N_4^+Cl^-$, 350.84 Dalton) and orange II sodium salt ($C_{16}H_{11}N_2O_4S^-Na^+$, 350.32 Dalton).



Formula (VI)

The polymeric membrane has a mean effective pore radius of 0.1-1 nm (e.g., 0.2-0.8 nm and 0.3-0.5 nm), a molecular weight cut off of 100 to 5000 Dalton (e.g., 200-2000 Dalton and 300-600 Dalton), and a pure water permeability of 0.1 to 200 $Lm^{-2}bar^{-1}h^{-1}$ (e.g., 0.5 to 100 $Lm^{-2}bar^{-1}h^{-1}$ and 1 to 10 $Lm^{-2}bar^{-1}h^{-1}$). The mean effective pore radius is the radius of a solute that is 50% rejected by the membrane; the molecular weight cut off is the molecular weight of a solute that is 90% rejected

by the membrane; and the pure water permeability is the volume of water that passes through the membrane per unit time, per unit area and per unit transmembrane pressure, which is calculated by the equation described in Example 2 below.

In one embodiment, the polymeric membrane is a cylinder (e.g., a hollow fiber membrane) having an outside diameter of 0.05 to 100 mm (e.g., 0.05-20 mm, 0.2-20 mm, 0.2-10 mm, 1-5 mm, and 0.3-1 mm) and an inside diameter of 0.02 to 98 mm (e.g. 0.02-18 mm, 0.1-18 mm, 0.1-8 mm, 0.8-4 mm, and 0.2-0.8 mm).

Also within the scope of this invention is a method of preparing a polymeric membrane. This method includes the steps of (1) providing a support membrane having a first porous layer, a second porous layer, and a macrovoid layer between the first porous layer and the second porous layer; and (2) coating the support membrane with a thin film layer by interfacial polymerization to obtain a polymeric membrane. The support membrane can be made by known methods. See, e.g., Pereira et al., Journal of Membrane Science, 192, 11-26 (2001); and Sun et al., AIChE Journal, 56, 1481-94 (2010). The thin film layer can also be prepared by known methods. See, e.g., Sun et al., Environmental Science and Technology, 45, 4003-09 (2011); Setiawan et al., Journal of Membrane Science, 369, 196-205 (2011); Ba et al., Journal of Membrane Science, 327, 49-58 (2009); Albrecht et al., Macromolecular Chemistry and Physics, 204, 510-21 (2003); Chiang et al., Journal of Membrane Science, 326, 19-26 (2009); and Kosaraju et al., Journal of Membrane Science, 321, 155-61 (2008).

The specific examples below are to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. Without further elaboration, it is believed that one skilled in the art can, based on the description herein, utilize the present invention to its fullest extent. All publications cited herein are incorporated by reference in their entirety.

EXAMPLE 1

A number of polymeric membranes were prepared following the below-described procedures.

Fabrication of three-layered hollow fiber supports

Three-layered hollow fiber supports were fabricated by a co-extrusion technique using a tri-channel spinneret. An outer dope, an inner dope, and a bore fluid were fed into the outside, the inside, and the middle channels of the spinneret,

respectively, by three ISCO syringe pumps. The spinneret had a length of 0.8 cm.

The outside channel had an outside diameter (OD) of 2.0 mm and an inside diameter (ID) of 1.74 mm; the inside channel had an OD of 1.58 mm and an ID of 1.0 mm; and the middle channel had a diameter of 0.84 mm. After the dopes and the bore fluid passed the spinneret, they met at the tip of the spinneret, passed through an air gap of 2.5 cm, entered a coagulation solvent, i.e., water, and were allowed to pass through a 2-meter long water bath to obtain a hollow fiber support, which were collected by a take-up drum. The detailed conditions are summarized in Table 1.

The as-spun hollow fiber supports were rinsed in a clean water bath for 3 days to remove the residual solvent. They were divided into two groups for post-treatments. One group was dipped in a 30 wt% glycerol aqueous solution for 2 days and dried in air at room temperature for further interfacial polymerization and nanofiltration experiments. The other group was directly freeze dried for morphological characterizations.

Table 1. Spinning conditions of three-layered hollow fiber supports

Outer dope composition (wt%):	PAI/Methano/NMP: 20.0/10.0/70.0
Inner dope composition (wt%):	PAI/PEG2K/NMP: 15.0/5.0/80.0
Bore fluid composition (wt%):	NMP/Water=80/20
External coagulant:	Water
Outer dope flow rate (ml/min)	0.5
Inner dope flow rate (ml/min)	4.0
Bore fluid flow rate (ml/min)	3.0
Air Gap (cm)	2.5
Take-up speed (m/min)	10
Spinneret dimension (mm):	0.84/1.0/1.58/1.74/2.0
Spinneret temperature (°C):	26

The morphology of the three-layered hollow fiber support was characterized by scanning electron microscope SEM. The results show that the outside diameter was around 860 μm and the inside diameter was around 660 μm . The cross-section of the membrane was asymmetric and included three layers: (1) a sponge-like and defect-free fist layer with a thickness less than 1 μm , located at the outer edge of the support; (2) a 100- μm -thick middle layer is full of large finger-like macrovoids; and (3) a sponge-like and porous second layer with a thickness of 5 to 10 μm to

withstand high pressures under NF operations.

Interfacial polymerization of the three-layered hollow fiber supports

Thin-film composite membranes were prepared via interfacial polymerization of HPEI in aqueous phase and IPC in organic phase (i.e., n-hexane).

- 5 The molecular weight and concentration of HPEI are shown in Table 3 below. The reaction was carried out at the outer surface of the hollow fiber membranes. First, the hollow fiber support was flushed with water to remove any residual glycerol. Second, a HPEI solution was flowed through the outside surface of the hollow fiber support with a peristaltic pump at 100 mL/min for 1 hour. Excessive HPEI solution
- 10 was drained and the support was dried in air for 5 minutes. Third, an IPC solution was flowed through the outside surface of the hollow fiber support for 3 minutes to form a thin film layer. Excessive IPC was drained. Finally, the polymeric membrane thus obtained was cured in an oven at 110 °C for 10 minutes. It was stored in water before nanofiltration tests.

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EXAMPLE 2

The polymeric membranes and the hollow fiber supports prepared in Example 1 were tested for nanofiltration as described below.

Nanofiltration test of the interfacial polymerized membranes

- 20 A laboratory-scale nanofiltration was set-up, including a feed reservoir, a pump, and a hollow fiber module. The pump sent a feed from the reservoir to the hollow fiber module. Every module contained 15 hollow fiber membranes with an effective area of around 60 cm². The feed solution was pumped into the outside surfaces of the hollow fiber and the permeate exited from the lumen. Before testing,
- 25 the hollow fiber membranes were conditioned at 6 bar for 6 hours. Further, they were subjected to a pure water permeation experiment at a constant flow rate of 1.5 L/minute at 5 bar to measure their pure water permeabilities (i.e., PWP, Lm⁻² bar⁻¹ h⁻¹), rejections and MWCO. A PWP was calculated using the equation

$$\text{PWP} = \frac{Q}{\Delta P \cdot A},$$

- 30 in which Q is the water permeation volumetric flow rate (L/h), A is the effective filtration area (m²), and ΔP is the transmembrane pressure drop (bar).

Rejection (R) of a solute is calculated as follows: $R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100$,

where C_p is the solute concentration in permeate and C_f is the solute concentration in the feed solution.

The polymeric membranes were tested in solute separation experiments with four types of solutions, namely, (1) 200 ppm neutral organic solutes (listed in Table 2 below) in water at pH 5.75 to measure pore size, pore size distribution, and MWCO (the hollow fiber supports were tested in these solutions as well); (2) four salt solutions (i.e., Na_2SO_4 , MgSO_4 , NaCl , and MgCl_2) at 1 mM at pH 5.75 to study the charge properties of the polymeric membranes (the hollow fiber supports were tested in these solutions as well); (3) 50 ppm positively charged (safranin O) or negatively charged (orange II sodium salt) dye solutions at pH 5.75 to test the decolourization capabilities of the interracially polymerized membranes (see Table 5); and (4) 200 ppm cephalexin solutions with various pH from 3 to 9, adjusted by NaOH (1.0 M) or HCl (1.0 M) solutions, to study the removal efficiency of this pharmaceutical active compound by the polymeric membranes as a function of pH (see Example 5). In each of the experiments, a feed solution was circulated at 5 bar for 1 hour before the concentrations of both the feed and the permeate were measured.

Table 2 shows the diffusivities and Stokes radii of nine neutral solute aqueous solutions for the polymeric membranes and the hollow fiber supports. The calculation of Stokes radii and pore size distribution is described in Sun et al., AICHE Journal, 56, 1481-94 (2010).

Table 2. Diffusivities and Stokes radii of neutral solutes in aqueous solutions (at 25°C)

Solute	MW [g·mol ⁻¹]	D_s [$\times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$]	r_s [nm]
<i>Solutes used for calculating the pore size of NF membranes:</i>			
Glycerol	92	0.78	0.260
Glucose	180	0.67	0.365
<u>Saccharose</u>	342	0.52	0.471
<u>Raffinose</u>	504	0.42	0.584
<i>Solutes used for calculating the pore size of the support:</i>			
PEG 2K	2 000	-	1.15
PEG 10K	10 000	-	2.82
PEG 20K	20 000	-	4.16
PEG 35K	35 000	-	5.68
PEO 100K	100 000	-	8.99

In this table, D_s stands for the diffusivities of the solutes and r_s stands for the Stokes radii of the solutes. Glycerol, glucose, saccharose, and raffinose are used for characterizing the pore size of the polymeric membranes, while PEG 2K, PEG 10K, PEG 20K, PEG 35K, and PEO 100K are used to characterize the pore size of the hollow fiber supports.

Effects of molecular weight and concentration of HPEI on NF performance

HPEIs with different molecular weights were used to prepare the thin film layer of the polymeric membrane. It was found that membranes made from various HPEIs demonstrated significant difference in rejections and PWP. Table 3 below shows the effects of HPEI molecular weight and concentration on nanofiltration performance of the polymeric membranes. As the molecular weight of HPEI increased from 2000 to 60000, the rejections of organic and inorganic solutes increased while the pure water permeability decreased, indicating the pore size became smaller. Increasing HPEI concentration resulted in increased rejections and decreased pure water permeabilities.

Table 3. Effects of molecular weight and concentration of HPEI

HPEI MW (Da)	HPEI concentration (wt%)	IPC concentration (wt%)	PWP ($\text{lm}^2\text{bar}^{-1}\text{h}^{-1}$)	Raffinose rejection (%)	MgCl ₂ rejection (%)
HPEI_2K	1	0.5	8.17	79.32	83.05
HPEI_60K	1	0.5	5.87	86.29	92.55
HPEI_60K	2	0.5	4.85	90.01	96.17
HPEI_60K	4	0.5	1.91	91.36	96.99

Raffinose concentration: 200ppm, MgCl₂ concentration: 1mM. pH 5.75. Pressure: 5 bar.

EXAMPLE 3

Characterization was carried out for the polymeric membranes and the hollow fiber supports, both prepared in Example 1. Their performances were measured and compared.

Characterizations of the polymeric membranes

The membranes and the hollow fiber support were photographed and measured by a field-emission scanning electron microscope (FESEM) and an atomic force microscope (AFM). As shown in FESEM photographs and AFM

photographs, the outer surfaces of the hollow fiber supports were quite smooth, with a mean roughness of $R_a=0.99\pm0.15$ nm. No nodule was observed even under $\times 100,000$ magnification. On the other hand, the photographs of the membranes clearly showed nodules with a size of 20 to 50 nm and a mean roughness of $R_a=3.00\pm0.30$ nm.

Water contact angels were measured by a Sigma 701 Tensiometer from KSV Instruments Limited. The water contact angle of the hollow fiber supports was $56.0\pm4.5^\circ$, much lower than that of our previously reported PAI hollow fiber membrane, i.e. $87.9\pm2.5^\circ$. See Sun et al., Environmental Science and Technology, 45, 4003-09 (2011). The water contact angle of the membrane was $41.7\pm0.5^\circ$, comparable to that of commercial hydrophilic nanofiltration membranes, for example, Desal5DL. See Boussu et al., Journal of Membrane Science, 310, 51-65 (2008).

Performance comparison of the polymeric membranes and the hollow fiber supports

The polymeric membranes and the hollow fiber supports were tested for nanofiltration of various organic solutes listed in Table 2 above.

The results of r_p , σ_p , MWCO, and PWP are summarized in Table 4 below. In this table, Bef IP refers to the hollow fiber supports; Aft IP refers to the polymeric membranes; r_p is the mean effective pore radius; and σ_p is the standard deviation, i.e., the ratio of r_s at the rejection of 84.13% to that at the rejection of 50%.

Table 4. Comparison of the polymeric membranes and the hollow fiber supports

ID	$\bar{r}_p$ (nm)	σ_p (-)	MWCO (Da)	PWP ($\text{lm}^2\text{bar}^{-1}\text{h}^{-1}$)
Bef IP	2.82	1.89	42602	43.25
Aft IP	0.36	1.44	489	4.85

(The feed solution concentration: 200ppm, pH 5.75. Pressure: 5 bar)

As shown in Table 4 above, the hollow fiber supports had a mean effective pore radius about 2.82 nm and a MWCO around 46202 Dalton. The polymeric membranes had a sharp pore size distribution with an unexpectedly low mean effective pore radius of 0.36 nm and an unexpectedly low MWCO of 489 Dalton.

Almost 100% of the pores were smaller than 1 nm. Further, the polymeric membranes showed an unexpectedly high PWP, i.e. $4.85 \text{ L m}^{-2} \text{ bar}^{-1} \text{ h}^{-1}$. Not being bound by any theory, interfacial polymerization of HPEI and IPC formed a polymer that eliminated defect or large pores on surfaces of the hollow fiber supports.

5 The polymeric membranes prepared in Example 1 had a positive charge in their thin film layer and a negative charge in their hollow fiber supports. The charge properties were characterized by testing the rejections of four electrolytes at 1 mM, pH 5.75, and 5 bars. The salt rejections of the hollow fiber supports decreased in the order Na_2SO_4 (22.89%), MgSO_4 (14.53%), NaCl (7.53%), and
 10 MgCl_2 (4.06%), indicating that the hollow fiber supports were negatively charged at neutral pH, according to the Donnan exclusion principle. By contrast, the order of salt rejections was unexpectedly reversed in the polymeric membranes, e.g., MgCl_2 (96.17%), NaCl (81.95%), MgSO_4 (85.49%), and Na_2SO_4 (60.26%). In other words, the polymeric membranes had a rejection of the divalent cation Mg^{2+} higher than
 15 that of the monovalent cation Na^+ , and a rejection of the divalent anion SO_4^{2-} lower than that of the monovalent anion Cl^- . This order was mainly determined by the Donnan exclusion effect, supporting the conclusion that that the membranes had a positive charge in the thin film layer. Moreover, the polymeric membranes had unexpectedly high rejections for MgCl_2 , NaCl , and MgSO_4 , likely through a
 20 stronger steric hindrance effect by the dense thin film layer.

EXAMPLE 4

The polymeric membranes prepared in Example 1 were tested to filter aqueous solutions of saccharose (0.2 g/L) and two dyes, i.e., safranin O
 25 ($\text{C}_{20}\text{H}_{19}\text{N}_4^+\text{Cl}^-$; 350.84 Dalton; 0.05 g/L; positively charged) and orange II sodium salt ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_4\text{S}^- \text{Na}^+$; 350.32 Dalton; 0.05 g/L; negatively charged).

Unexpectedly, the rejection of safranin O was as high as 99.8% and the rejection of orange II was as high as 98.75%. The normalized water flux, which is the ratio of permeate flux of the dye solution, J ($\text{L m}^{-2} \text{ h}^{-1}$), to the pure water flux, J_0 (L m^{-2}
 30 h^{-1}), were shown in Table 5 below. Orange II sodium salt had a normalized water flux lower than those of safranin O and saccharose, implying that certain amount of orange II was retained in the thin film layer, which further increased the rejection.

These polymeric membranes effectively removed dyes from their aqueous solutions.

Table 5. Filtration of safranin O, orange II and saccharose

Solute	Safranin O	Orange II sodium salt	Saccharose
Molecular formula	$C_{20}H_{19}N_4^+Cl^-$	$C_{16}H_{11}N_2O_4S_7Na^+$	$C_{12}H_{22}O_{11}$
MW (Da)	350.84	350.32	342.30
Size (nm ³)	$1.10 \times 0.95 \times 0.49$	$1.10 \times 0.63 \times 0.70$	$1.05 \times 0.66 \times 0.73$
Rejection, (%)	99.80	98.75	76.39
Flux, (L m ⁻² h ⁻¹)	22.71	20.60	21.35
J/J_0 , (%)	93.65	84.95	88.04

 $J_0=24.25 \text{ L m}^{-2}\text{h}^{-1}$

Further, the polymeric membranes were tested to recycle water from the two water samples obtained from two textile factories. Unexpectedly, the color of both water samples was effectively removed. Namely, the color ADMI value of water Sample 1 decreased from 390 ADMI to 20 ADMI and the color ADMI value of water Sample 2 decreased from 429 ADMI to 29 ADMI. See Table 6 below. The polymeric membranes can be used to decolorize and recycle dye waste water.

Table 6. Color removal efficiency

	Sample 1	Sample 2
Color before filtration (ADMI)	390	429
Color after filtration (ADMI)	20	29
Color removal efficiency (%)	94.9	93.215

EXAMPLE 5

The polymeric membranes prepared in Example 1 were tested to filter cephalixin aqueous solution.

Cephalixin, a widely used antibiotic, is a zwitterion. The rejection of cephalixin by the hollow fiber supports was below 20% in pH 2-8. By contrast, the rejection of cephalixin by the polymeric membrane was unexpectedly as high as 95.5 %. Interestingly, pH had a big effect on cephalixin rejections. As pH increased from 2 to 8, the cephalixin rejections decreased from 95.5 % to 77.2 %. Note that cephalixin is positively charged at pH 2, and is negatively charged at pH 8. The polymeric membranes showed a rejection of cephalixin higher at low pH than at high pH, which agrees with the Donnan exclusion principle.

OTHER EMBODIMENTS

All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the same, equivalent, or similar purpose. Thus, unless
5 expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

From the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to
10 adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

WHAT IS CLAIMED IS:

1. A polymeric membrane for nanofiltration, the membrane comprising:
a macrovoid layer, with a pore size of 0.001 to 100 μm and a thickness of 20
5 to 2000 μm , having a first side and a second side;
a first porous layer, with a pore size of 0.1 to 200 nm and a thickness of 0.01
to 20 μm , covering the first side of the macrovoid layer;
a second porous layer, with a pore size of 0.001 to 100 μm and a thickness of
1 to 20 μm , covering the second side of the macrovoid layer; and
10 a thin film layer, with a pore size of 0.1 to 10 nm and a thickness of 0.001 to 2
 μm , covering the first porous layer,
wherein the polymeric membrane has a molecular weight cut off of 100 to 5000
Dalton and a pure water permeability of 0.1 to 200 $\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$.

15 2. The membrane of claim 1, wherein the thin film layer has a positive or
negative charge, and the first porous layer has a charge opposite to that of the thin
film layer.

3. The membrane of claim 2, wherein
20 the first porous layer is made of polyamide, polyimide, sulphonated
polyimides, polyamide-imide, sulphonated polyethersulphone, sulphonated
polysulphone, polybenzimidazole, polyethersulphone, polysulphone, cellulose acetate,
polyacrylonitrile, polyether ether ketone, sulphonated polyether ether ketone, or a
combination thereof;

25 each of the macrovoid layer and the second porous layer is, independently,
made of cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose
propionate, cellulose butyrate, cellulose acetate propionate, cellulose dibutyrate,
cellulose tributyrates, polyacrylonitrile, polyvinyl alcohol, polyamide, polyimide,
sulphonated polyimides, polyamide-imide, sulphonated polyethersulphone,
30 sulphonated polysulphone, polybenzimidazole, polyvinylidene difluoride,
polyethersulphone, polysulphone, polytetrafluoroethylene, polyether ether ketone,
sulphonated polyether ether ketone, or a combination thereof; and

the thin film layer is made of polyamide, polyamide-imide, or a combination
thereof.

4. The membrane of claim 3, wherein each of the macrovoid layer, the first porous layer, and the second porous layer is made of polyamide-imide; and the thin film layer is made of hyperbranched polyethylene isophthaloylamide.

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5. The membrane of claim 4, wherein the membrane has a molecular weight cut off of 200 to 2000 Dalton and a pure water permeability of 0.5 to $100 \text{ Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$, the macrovoid layer has a pore size of 0.01 to $1 \mu\text{m}$ and a thickness of 50 to $1000 \mu\text{m}$, the first porous layer has a pore size of 1 to 100 nm and a thickness of 0.1 to $10 \mu\text{m}$, the second porous layer has a pore size of 0.01 to $1 \mu\text{m}$ and a thickness of 1 to $20 \mu\text{m}$, and the thin film layer has a pore size of 0.2 to 5 nm , a thickness of 0.01 to $1 \mu\text{m}$.

6. The membrane of claim 5, wherein the membrane has a molecular weight cut off of 300 to 600 Dalton and a pure water permeability of 1 to $10 \text{ Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$, the macrovoid layer has a pore size of 0.05 to $0.1 \mu\text{m}$ and a thickness of 80 to $200 \mu\text{m}$, the first porous layer has a pore size of 5 to 20 nm and a thickness of 0.5 to $5 \mu\text{m}$, the second porous layer has a pore size of 0.1 to $0.5 \mu\text{m}$ and a thickness of 2 to $10 \mu\text{m}$, and the thin film layer has a pore size of 0.3 to $1 \mu\text{m}$, a thickness of 0.05 to $0.2 \mu\text{m}$.

7. The membrane of claim 3, wherein the membrane has a molecular weight cut off of 200 to 2000 Dalton and a pure water permeability of 0.5 to $100 \text{ Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$, the macrovoid layer has a pore size of 0.01 to $1 \mu\text{m}$ and a thickness of 50 to $1000 \mu\text{m}$, the first porous layer has a pore size of 1 to 100 nm and a thickness of 0.1 to $10 \mu\text{m}$, the second porous layer has a pore size of 0.01 to $1 \mu\text{m}$ and a thickness of 1 to $20 \mu\text{m}$, and the thin film layer has a pore size of 0.2 to 5 nm , a thickness of 0.01 to $1 \mu\text{m}$.

8. The membrane of claim 7, wherein the membrane has a molecular weight cut off of 300 to 600 Dalton and a pure water permeability of 1 to $10 \text{ Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$, the macrovoid layer has a pore size of 0.05 to $0.1 \mu\text{m}$ and a thickness of 80 to $200 \mu\text{m}$, the first porous layer has a pore size of 5 to 20 nm and a thickness of 0.5 to 5

μm , the second porous layer has a pore size of 0.1 to 0.5 μm and a thickness of 2 to 10 μm , and the thin film layer has a pore size of 0.3 to 1 μm , a thickness of 0.05 to 0.2 μm .

5 9. The membrane of claim 2, wherein the membrane has a molecular weight cut off of 200 to 2000 Dalton and a pure water permeability of 0.5 to 100 $\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$, the macrovoid layer has a pore size of 0.01 to 1 μm and a thickness of 50 to 1000 μm , the first porous layer has a pore size of 1 to 100 nm and a thickness of 0.1 to 10 μm , the second porous layer has a pore size of 0.01 to 1 μm and a thickness of 1 to 20 μm , and the thin film layer has a pore size of 0.2 to 5 nm, a thickness of 0.01 to 1 μm .

10 10. The membrane of claim 9, wherein the membrane has a molecular weight cut off of 300 to 600 Dalton and a pure water permeability of 1 to 10 $\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$, the macrovoid layer has a pore size of 0.05 to 0.1 μm and a thickness of 80 to 200 μm , the first porous layer has a pore size of 5 to 20 nm and a thickness of 0.5 to 5 μm , the second porous layer has a pore size of 0.1 to 0.5 μm and a thickness of 2 to 10 μm , and the thin film layer has a pore size of 0.3 to 1 μm , a thickness of 0.05 to 0.2 μm .

20 11. The membrane of claim 1, wherein the membrane is a cylinder and has an outside diameter of 0.05 to 20 mm, the thin film layer being the outer layer of the cylinder.

25 12. The membrane of claim 11, wherein the thin film layer has a positive or negative charge, and the first porous layer has a charge opposite to that of the thin film layer.

30 13. The membrane of claim 12, wherein the first porous layer is made of polyamide, polyimide, sulphonated polyimides, polyamide-imide, sulphonated polyethersulphone, sulphonated polysulphone, polybenzimidazole, polyethersulphone, polysulphone, cellulose acetate,

polyacrylonitrile, polyether ether ketone, sulphonated polyether ether ketone, or a combination thereof;

each of the macrovoid layer and the second porous layer is, independently, made of cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose dibutyrate, cellulose tributyrates, polyacrylonitrile, polyvinyl alcohol, polyamide, polyimide, sulphonated polyimides, polyamide-imide, sulphonated polyethersulphone, sulphonated polysulphone, polybenzimidazole, polyvinylidene difluoride, polyethersulphone, polysulphone, polytetrafluoroethylene, polyether ether ketone, sulphonated polyether ether ketone, or a combination thereof; and

the thin film layer is made of polyamide, polyamide-imide, or a combination thereof.

14. The membrane of claim 13, wherein each of the macrovoid layer, the first porous layer, and the second porous layer is made of polyamide-imide; and the thin film layer is made of polyisophthalamine-polyethyleneimine.

15. The membrane of claim 14, wherein the membrane has an outside diameter of 0.2 to 10 mm, a molecular weight cut off of 200 to 2000 Dalton, and a pure water permeability of 0.5 to 100 $\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$; the macrovoid layer has a pore size of 0.01 to 1 μm and a thickness of 50 to 1000 μm ; the first porous layer has a pore size of 1 to 100 nm and a thickness of 0.1 to 10 μm ; the second porous layer has a pore size of 0.01 to 1 μm and a thickness of 1 to 20 μm ; and the thin film layer has a pore size of 0.2 to 5 nm and a thickness of 0.01 to 1 μm .

16. The membrane of claim 15, wherein the membrane has an outside diameter of 0.3 to 1 mm, a molecular weight cut off of 300 to 600 Dalton, and a pure water permeability of 1 to 10 $\text{Lm}^{-2}\text{bar}^{-1}\text{h}^{-1}$; the macrovoid layer has a pore size of 0.05 to 0.1 μm and a thickness of 80 to 200 μm ; the first porous layer has a pore size of 5 to 20 nm and a thickness of 0.5 to 5 μm ; the second porous layer has a pore size of 0.1 to 0.5 μm and a thickness of 2 to 10 μm ; and the thin film layer has a pore size of 0.3 to 1 μm and a thickness of 0.05 to 0.2 μm .

17. The membrane of claim 13, wherein the membrane has an outside diameter of 0.2 to 10 mm, a molecular weight cut off of 200 to 2000 Dalton, and a pure water permeability of 0.5 to 100 Lm⁻²bar⁻¹h⁻¹; the macrovoid layer has a pore size of 0.01 to 1 μm and a thickness of 50 to 1000 μm; the first porous layer has a pore size of 1 to 100 nm and a thickness of 0.1 to 10 μm; the second porous layer has a pore size of 0.01 to 1 μm and a thickness of 1 to 20 μm; and the thin film layer has a pore size of 0.2 to 5 nm and a thickness of 0.01 to 1 μm.

18. The membrane of claim 17, wherein the membrane has an outside diameter of 0.3 to 1 mm, a molecular weight cut off of 300 to 600 Dalton, and a pure water permeability of 1 to 10 Lm⁻²bar⁻¹h⁻¹; the macrovoid layer has a pore size of 0.05 to 0.1 μm and a thickness of 80 to 200 μm; the first porous layer has a pore size of 5 to 20 nm and a thickness of 0.5 to 5 μm; the second porous layer has a pore size of 0.1 to 0.5 μm and a thickness of 2 to 10 μm; and the thin film layer has a pore size of 0.3 to 1 μm and a thickness of 0.05 to 0.2 μm.

19. A method of rejecting a substance in a liquid, the method comprising: providing a mixture of a substance and a liquid, in which the substance has a charge, a molecular weight over 100 Dalton, a particle size over 0.3 nm, or a combination thereof; and the liquid is neutral and has a molecular weight below 100 Dalton; and

bringing the mixture in contact with a membrane of claim 1 so as to allow the liquid to pass through the membrane, whereby rejecting the substance on the membrane via size exclusion, Donnan exclusion, or both.

20. A method of preparing a polymeric membrane, the method comprising: providing a support membrane having a first porous layer, a second porous layer, and a macrovoid layer between the first porous layer and the second porous layer; and

coating the support membrane with a thin film layer by interfacial polymerization to obtain a polymeric membrane.