THIN FILM COMPOSITE OSMOSIS MEMBRANES

Field of the Invention

The present invention relates to a thin film composite membrane that has high flux and that is useful for applications of forward osmosis (also know as osmosis and direct osmosis), pressure-retarded osmosis and other low-pressure-driven liquid filtration, and a method for producing the same, and more particularly, to a forward osmosis membrane having a salt rejection 99+% or greater, and comprising an asymmetric porous support membrane and a thin skin layer. The membranes of the present invention find use in a variety of applications including osmotic-driven water purification and filtration, desalination of seawater, purification and filtration of contaminated aqueous waste streams, pressure-retarded osmosis for power generation and the like.

Background of the Invention

Salt rejecting membranes for reverse osmosis applications have been prepared for more than 40 years. Cellulose-based membranes for reverse osmosis were firstly fabricated by an immersion precipitation process. Subsequently, thin film composite (TFC) polyamide membranes were fabricated by an interfacial copolymerization method and have been widely used for filtration, such as in the field of desalination.

The past 45 years of development of highly selective membranes has been focused primarily on the reverse osmosis process. Reverse osmosis (RO) is a pressure driven process. That is, once the osmotic pressure of the solution is overcome, the primary resistance to water flux through the membrane is hydrodynamic. This means the friction of water flowing through the pores of the membrane is the primary flow resistance. In RO membranes, the flow resistance is almost entirely in the thin dense surface layer (also known as “rejection layer” or “skin layer”) and the microporous support layer and fabric backing have a minor or insignificant resistance. TFC membrane showed higher flux and rejection than cellulose-based membrane when used in RO process because TFC membrane

has thinner skin layer and more porous support layer. Particularly the performances of TFC membranes can be adjusted by modifying the two different layers independently.

Forward osmosis (FO), also commonly known as osmosis or direct osmosis, by contrast, is a diffusion driven process instead of pressure driven process, so the factors affecting water flux are dramatically different than reverse osmosis. In FO process, a solution of considerably high concentration (known as draw solution) is utilized to generate a hydrostatic osmotic pressure gradient across a semi-permeable membrane to extract freshwater from a feed solution (such as seawater, brine or any waste stream), which is on the other side of the membrane. Since this process capitalizes the phenomenon of natural osmosis, little energy and thus, lower cost is required as compared to traditional technologies. The FO membrane can be made much thinner than the other kinds of membrane due to the minimal hydraulic pressure applied at the feed side. In FO process, the internal concentration polarization (ICP) has significantly negative effect on the water flux because the pores in the support layer trap ions. Increasing the porosity, particularly the pore size can favour the convective diffusion of ion in and out of the pores. Because of the reasons mentioned above, a high performance FO membrane requires a dramatically different structure than the RO membranes. A recent report has demonstrated how an ideal FO membrane should be (Ng et al., 2006), which should be as thin as possible and have a high porous support layer while achieving high rejection of salts and dissolved compounds. At this point in time, FO membranes available commercially are made of cellulose-based polymer by immersion precipitation process. In terms of thin-skin-layer and high-porous-support-layer, TFC membranes have a potential to further enhance the performances and durability of FO membranes.

Summary of the Invention

In view of the above, the present invention is intended to produce a thin film composite osmosis membrane with better performances in terms of water flux and salt rejection.

The concept of modifying the structure of support layer of TFC membrane, such as decreasing thickness and increasing porosity and pore size, to improve performance, particularly specific permeate flux and high salt rejection, has been demonstrated in this invention for the case of FO membranes.

The concept can be applied in fabrication of membrane with different polymeric materials to produce a membrane of different targeted pore size and forms (tube, hollow fiber or flat sheet), i.e., not restricted to only FO flat sheet membranes.

The present invention provides such a FO membrane comprising of a supported porous membrane and a skinned layer (thin film layer), which exhibits the benefits of a high dissolved compounds retention, low resistance to water diffusion, lack of defects, and good structural integrity. The present invention also provides a method for preparing such a membrane.

Specifically, the present invention provides a thin film composite FO membrane having three layers comprising:

(a) a ultra-thin film layer (or skinned layer), which is usually made of polyamide and formed by interfacial copolymerization of a polyfunctional amine solution and a polyfunctional acid halide solution on the surface of a porous layer, as a rejection surface of the forward osmosis membrane;

(b) a porous support layer bound to the bottom surface of the skin layer, wherein the layer is a separated membrane and made from some polymeric material by immersion precipitation process; and

(c) a mesh or non-woven fabric embedded within the porous support layer.

The present invention further provides an immersion/precipitation process for making the support porous membrane comprising:

(a) applying a casting solution slurry of polymeric material in a solvent onto a surface of a rotating drum to form a casting solution layer, wherein the casting solution comprises from about 70% to about 95% (by volume) of a solvent formulation and from about 5% to about 30% (by volume) of a polymeric material;

(b) pulling a non-woven fabric or woven mesh support material into the casting solution slurry on the surface of the rotating drum so that the support material is fully embedded within the casting solution slurry; and

(c) immersing the casting solution-imbedded support material into a water bath, whereby the casting solution-imbedded support material coagulates the polymeric material into a support membrane for forward osmosis membrane.

Preferably, the skinned layer is ultra-thin and has an average thickness of less than 10 micrometers. Preferably, the support layer has an average thickness from about 40 to about 200 micrometers.

Preferably, the mesh is a woven monofilament mesh. Preferably, the woven mesh is selected from the group consisting of polyester woven screens, polypropylene woven screens, woven acrylics, woven nylon screens, and combinations thereof.

Preferably, the non-woven fabric is selected from the group consisting of polyester, polypropylene, polyolefin blends polyester-polyolefin composites, and nylon.

Preferably, the polymeric membrane material from which the support layer is made is selected from the group consisting of polyethersulfones, polyphenylenesulfones, polyphenylenesulfidesulfones, polyacrylonitriles, cellulose esters, polyphenyleneoxides, polypropylenes, polyvinyledenefluoride, polyvinylchlorides, polyarylsulfone, polyphenylene sulfone, polyetheretherketone or polysulphone, and combinations thereof.

Preferably, the solvent formulation comprises acetone, chloroform, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone, tetrahydrofuran.

In one aspect, there is provided a membrane including: a support layer; a mesh formed in the support layer; and a rejection layer formed on the support layer.

Preferably, the mesh has an open area of more than 50 percent (%).

Preferably, the mesh is a monofilament mesh.

Preferably, the support layer has a thickness of between about 45 micrometers (μm) and about 150 μm.

Preferably, the mesh has a thickness of between about 50 μm and about 150 μm.

In another aspect, there is provided a method of manufacturing a support layer of a membrane, including: preparing a polymer solution; contacting a mesh with the polymer solution; and coagulating the polymer solution contacting the mesh.

In yet another aspect, there is provided a method of manufacturing a membrane, including: preparing a polymer solution; contacting a mesh with the polymer solution; coagulating the polymer solution contacting the mesh to form a support layer; and forming a rejection layer on the support layer.

Preferably, the polymer solution comprises between about 70% and about 95% (by volume) of a solvent.

Preferably, the solvent is selected from a group consisting of acetone, chloroform, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone and tetrahydrofuran.

Preferably, the polymer solution comprises between about 5% and about 30% (by volume) of a polymeric material.

In one aspect, there is provided a thin film composite forward osmosis membrane having three layers comprising: (a) a ultra-thin film layer as skin layer, which is usually polyamide and formed by interfacial copolymerization of a polyfunctional amine solution and a polyfunctional acid halide solution on the surface of a porous layer, as a rejection surface of the forward osmosis membrane;(b) a porous support layer bond to the bottom surface of the skin layer, wherein the layer is a separated membrane and made from some polymeric material by immersion precipitation process; and (c) a mesh or nonwoven fabric embedded within the porous support layer.

Preferably, the skin layer has an average thickness of from about 3 to about 15 microns.

Preferably, the support layer has an average thickness of from about 40 to about 150 microns.

Preferably, the support fabric is a monofilament mesh.

Preferably, the woven mesh is selected from the group consisting of polyester woven screens, polypropylene woven screens, woven acrylics woven nylon screens, and combinations thereof.

Preferably, a semiporous membrane is provided as a support layer in the thin film composite membrane. Preferably, the polymeric membrane material is selected from the group consisting of polyethersulfones, polyphenylenesulfones, polyphenylenesulfidesulfones, polyacrylonitriles, cellulose esters, polyphenyleneoxides, polypropylenes, polyvinylchlorides, polyarylsulfone, polyphenylene sulfone, polyetheretherketone or polysulphone, and combinations thereof.

In another aspect, there is provided an immersion/precipitation process for making preparing the semiporous membrane. The process comprises: (a) providing a porous nonwoven or woven support material having greater than 30% open area; (b) applying a casting solution slurry onto a rotating drum to form a

casting solution layer having a substantially uniform surface, wherein the casting solution comprises from about 70% to about 95% (by volume) of a solvent formulation and from about 5% to about 30% (by volume) of a polymeric solid material; and (c) embedding the support fabric into the layer of casting solution by pulling the support into the layer; and (d) immersing the casting solution into a water bath to coagulate the polymeric material into a support membrane backed with the support material.

Preferably, the woven mesh is selected from the group consisting of polyester woven screens, polypropylene woven screens, woven acrylics woven nylon screens, and combinations thereof.

Preferably, the solvent formulation comprises acetone, chloroform, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone, tetrahydrofuran or mixtures thereof.

Other aspects and advantages of the invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, illustrating by way of example the principles of the invention.

Brief Description of the Drawings

The following detailed description of preferred embodiments of the invention will be better understood when read in conjunction with the appended drawings. The present invention is illustrated by way of example and is not limited by the accompanying figures, in which like references indicate similar elements.

FIG. 1 is a schematic diagram illustrating a cross section of the inventive membrane having a woven fabric (the grid-like pattern); and

FIG. 2 is a schematic diagram of one type of a laboratory-scale setup for testing a FO membrane.

Detailed Description of the Preferred Embodiments

A membrane and methods for forming the membrane and layers of the membrane are provided. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be understood, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail in order not to unnecessarily obscure the present invention.

The present invention provides a method of manufacturing a thin film composite FO membrane by interfacial copolymerizing a polyfunctional amine solution and a polyfunctional acid halide solution on the surface of a thin porous support membrane.

Each layer of the inventive membrane provides different properties to optimize FO performance in different types of applications. For example, the thin film layer is the site of rejection of salts, microbiological agents, biological molecules or other solid materials. The thin film layer is preferably less than 10 micrometers thick.

The porous membrane employed in the present invention for the support layer of FO membrane support may preferably have an asymmetric structure along the cross-sectional direction and is typically about 50 micrometers thick and is highly porous. The microporous membrane can be made by any suitable polymer. Examples of such polymers can be polyethersulfones, polyphenylenesulfones, polyphenylenesulfidesulfones, polyacrylonitriles, cellulose esters, polyphenyleneoxides, polypropylenes, polyvinylchlorides, polyarylsulfone, polyphenylene sulfone, polyetheretherketone or polysulphone.

Firstly, the membrane polymeric material is dissolved in a water-soluble solvent (non-aqueous) system to form a solution. Appropriate water-soluble solvent systems for support membranes include, for example, acetone, chloroform, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-

methylpyrrolidone, tetrahydrofuran or mixtures thereof. Included in the water-soluble solvent systems are additives (e.g., PEG and PVP). The solution is cast onto a rotating drum and an open fabric is pulled into the solution so that the fabric is embedded into the solution. The solution is then passed into the coagulation bath.

Briefly, casting a membrane involves a solution of membrane solids and solvent extruded over a drum to spread the solution out, wherein the drum is turning to allow even distribution of a thin layer of the polymer solution or slurry (solids suspended within a solvent). The drum can be made of any suitable material, including metals such as stainless steel, aluminium, aluminium alloy, iron, and plastics such as, Polytetrafluoroethylene (PTFE), Polypropylene (PP), Polyethylene (PE), PolyvinylChloride (PVC), Acrylonitrile Butadiene Styrene (ABS), Polyamide (PA), polyoxymethylene (POM), polycarbonate(PC), polyphenylene oxide (PPO), Polyester (PET), Polyethylene terephthalate (PETE).The solution is either applied to a fabric or it is first applied to a rotating drum and a support mesh or fabric is embedded into the solution or slurry. The membrane-forming material then rotates with the drum into a water bath to gel to form the membrane as a continuous process. Preferably, the polymeric slurry solution contains from about 5% to about 30% (by volume) solids, for polysulone polymer, the concentration of polysulfone in the microporous membrane may be for example between about 5 to about 20wt%.

The membrane actually forms when the polymer contacts the coagulation bath because bath makes the polymer solution unstable. Since the solution is 70% to 95% solvent, the polymer gels in a spongy microporous structure. The coagulation bath may contain water or a mixture of water and an additive as a solvent. The additive is selected from the group acetone, chloroform, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone, tetrahydrofuran or mixtures thereof.

The newly-formed membrane will cure in the water bath. During the curing process, the newly formed membrane is continually in contact with a roller and the

roller surface is in contact with second side of the membrane having a mesh backing material contained within. This arrangement to have a roller maintain contact with the second side of the backing material prevents a second skin from forming.

Next, a rinse (water) bath rinses out residual solvents. This is preferably followed by an anneal bath (at approximately 40-90°C) to allow a relaxation of polymer stress points to form a more uniform membrane.

Typically, the membrane has an overall thickness of 45 to 200 micrometers and the support fabric has a thickness from 50 to 200 micrometers. The support fabric preferably has over 50% open area.

The immersion/precipitation process forms an asymmetric membrane with highly porous support layer and allows diffusion of solids within the porous support layer. The support layer is created by the immersion/precipitation process and its porosity controlled by both the casting parameters and by the choices of solvent and ratio of solids of polymeric material to solvent solution.

The thus obtained polymeric porous substrate is immersed in an aqueous A polyfunctional amine solution for 0.5-10 min and then being taken out from the solution. After removing the liquid droplets on the surface of the substrate, a solution of polyfunctional acid halide is applied to the surface of the substrate for 0.5-10 min where interfacial copolymerization takes place at the interface between the two solutions, resulting in the formation of a polyamide thin film. Subsequently, the solvent remaining on the surface of the substrate is being evaporated. The thus prepared composite membrane is preferably washed with flowing water for 10-50 min to remove the non-reacted acid chloride. A curing process is then applied to the thus prepared composite membrane in hot water or air at 60-90°C for 2-20 min.

The polyfunctional amine employed in the process of the present invention is an aliphatic, aromatic, heterocyclic or alicyclic compound which has two or more primary or secondary amino groups in one molecule. Preferred examples of the

polyfunctional amine include m-phenylenediamine, p-phenylenediamine, piperazine, 2-methylpiperazine, N,N-dimethylethylenedlamine, 1,3,5-triaminobenzene and the like as well as mixtures thereof. The polyfunctional amine may preferably be in the form of aqueous solution when applied to the surface of the microporous substrate. Pure water is preferred as the solvent.

The polyfunctional acid halide employed in the process of the present invention is an aliphatic, aromatic, heterocyclic or alicyclic compound having two or more acyl halide groups in one molecule. Preferred examples of the polyfunctional acid halide include isophthaloyl chloride, terephthaloyl chloride, trimesoyl chloride, 1,2,4-benzenetricarboxylic acid trichloride and the like. The solvent employed for formulating a solution of the polyfunctional acid halide are preferred saturated aliphatic hydrocarbons and alicyclic hydrocarbons, including n-hexane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, cyclooctane, ethylcyclohexane, 1-octene and 1-decene, particularly ISOPAR series as well as mixtures thereof. Polyfunctional acid halide solution may preferably be 0.01 - 1% by weight.

The invention will now be described by way of examples thereof. It should be noted that the examples are presented for the illustration purpose only and should not be interpreted in any restrictive way.

The FO performance of the prepared membranes was evaluated in terms of pure water flux and solute rejection in a laboratory FO crossflow set-up (as shown in Fig. 2).

The specially designed cross-flow membrane cell (100) has a channel on each side of the membrane (104), which allows the feed (116) and draw (118) solutions to flow through separately. Each channel has dimensions of 4, 100, and 40 mm for channel height, length, and width, respectively. Cocurrent flow was used with flow rate in each channel controlled by a centrifugal pump (106) (Cole-Parmer, U.S.A.) and monitored with a flow meter (108) (Blue-white Industries Ltd., U.S.A.). The cross-flow rates for the feed and draw solution were both maintained at 2.0 $L*min^{-1}$ (equivalent to 8.34 $cm*s^{-1}$). Heaters were used to maintain the

temperature of the feed (116) and draw (118) solutions homogenously at 25°C. The solutions were stirred to keep them homogenous by stirrer (120). A weighing scale (112) (SB16001, Mettler Toledo, Germany) connected to a computer (114) was used to monitor the weight of water permeating through the membrane from the feed to the draw side, from which the water flux was calculated. In the experiments, 2.0M NaCl solution was used as the draw solution and deionized water as the feed solution. All membranes were tested in the orientation of the dense selective side facing the feed solution (FO mode).

The water flux was calculated from the changes in the weight of the draw solution during each experimental run. As water permeated through the membrane from the feed to the draw side, the weight of the draw solution increased with time. Water flux (Jw) can then be calculated:

$$J_{\mathrm{w}} = \frac{\Delta\ \mathrm{Weight}}{\mathrm{Water\ Density} \times \mathrm{Membrane\ Surface\ Area} \times \Delta\ \mathrm{Time}} \qquad (1)$$

To determine the NaCl rejection, a sample of feed solution was taken after a complete FO run and measured the chloride concentration using a chloride selective electrode (6560-10C, Horiba, Kyoto, Japan). Based on the amount of water passed into the draw solution over the course of the experiment and the final amount of NaCl in the feed solution, the permeate NaCl concentration is determined. The percent salt rejection, R, is then calculated from

$$R = (1 - \frac{C_p}{C_d}) \times 100\ \% \qquad (2)$$

where C_p and C_d are permeate and draw NaCl concentrations, respectively.

Example 1

In a polyester mesh (180mesh), 13wt% polysulfone with 5wt% PVP solution in NMP was cast to a thickness of about 100 μm and the resultant was immersed in water bath at room temperature so as to gel the polysulfone solution, thereby obtaining a mesh-embedded-reinforced polysulfone substrate. The thus

obtained polysulfone substrate was sufficiently washed with water so as to exchange the solvent in the substrate with water.

The thus obtained polysulfone microporous substrate was immersed in an aqueous m-phenylenediamine aolution(concentration: 2.0wt% with 0.1wt% sodium dodecyl benzosulfonate) for two minutes and then taken out from the solution. After removing the liquid drops on the surface of the substrate, a solution of trimesoyl chloride (concentration: 0.1wt%, solvent: hexane) was applied to the surface of the substrate for one minute. The thus prepared composite membrane was washed with flowing water for 10 minutes to remove the non-reacted acid chloride.

The thus prepared composite semipermeable membrane had a water flux of 13.76 GFD and salt rejection of 99.89%. Thus, the membrane had high performance (i.e., high water flux and salt rejection).

Example 2

In a polyester mesh (180mesh), 13wt% polysulfone with 5wt% PVP solution in NMP was cast to a thickness of about 200 μm and the resultant was immersed in water bath at room temperature so as to gel the polysulfone solution, thereby obtaining a mesh-embedded-reinforced polysulfone substrate. The thus obtained polysulfone substrate was sufficiently washed with water so as to exchange the solvent in the substrate with water.

The thus obtained polysulfone microporous substrate was immersed in an aqueous m-phenylenediamine aolution(concentration: 2.0wt% with 0.1wt% sodium dodecyl benzosulfonate) for two minutes and then taken out from the solution. After removing the liquid drops on the surface of the substrate, a solution of trimesoyl chloride (concentration: 0.1wt%, solvent: hexane) was applied to the surface of the substrate for one minute. The thus prepared composite membrane was washed with flowing water for 10 minutes to remove the non-reacted acid chloride.

The thus prepared composite semipermeable membrane had a water flux of 14.08 GFD and salt rejection of 99.92%.

Example 3

In a polyester mesh (180mesh), 15wt% polysulfone with 5wt% PVP solution in NMP was cast to a thickness of about 100μm and the resultant was immersed in water bath at room temperature so as to gel the polysulfone solution, thereby obtaining a mesh-embedded-reinforced polysulfone substrate. The thus obtained polysulfone substrate was sufficiently washed with water so as to exchange the solvent in the substrate with water.

The thus obtained polysulfone microporous substrate was immersed in an aqueous m-phenylenediamine aolution(concentration: 2.0wt% with 0.1wt% sodium dodecyl benzosulfonate) for two minutes and then taken out from the solution. After removing the liquid drops on the surface of the substrate, a solution of trimesoyl chloride (concentration: 0.1wt%, solvent: hexane) was applied to the surface of the substrate for one minute. The thus prepared composite membrane was washed with flowing water for 10 minutes to remove the non-reacted acid chloride.

The thus prepared composite semipermeable membrane had a water flux of 15.83GFD and salt rejection of 99.85%.

Example 4

The production conditions were exactly the same as in Example 3 except for the thickness of the membrane being 200 μm.

The thus prepared composite semipermeable membrane had a water flux of 18.17 GFD and salt rejection of 99.84%.

While the preferred embodiments of the invention have been illustrated and described, it will be clear that the invention is not limited to these embodiments only. Numerous modifications, changes, variations, substitutions and equivalents

will be apparent to those skilled in the art without departing from the scope of the invention as described in the claims. For example, the application of the thin support membrane is not limited to the fabrication of FO membranes. It can extend to nanofiltration membrane, ultrafiltration membrane and microfiltration membrane.

Further, unless the context dearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising" and the like are to be construed in an inclusive as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

CLAIMS

1. A membrane, comprising:
a support layer;
a mesh formed in the support layer; and
a rejection layer formed on the support layer.

2. The membrane of claim 1, wherein the mesh has an open area of more than 50 percent (%).

3. The membrane of claim 1, wherein the mesh is a monofilament mesh.

4. The membrane of claim 1, wherein the support layer has a thickness of between about 45 micrometers (μm) and about 150 μm.

5. The membrane of claim 1, wherein the mesh has a thickness of between about 50 μm and about 150 μm.

6. A method of manufacturing a support layer of a membrane, comprising:
preparing a polymer solution;
contacting a mesh with the polymer solution; and
coagulating the polymer solution contacting the mesh.

7. A method of manufacturing a membrane, comprising:
preparing a polymer solution;
contacting a mesh with the polymer solution;
coagulating the polymer solution contacting the mesh to form a support layer; and
forming a rejection layer on the support layer.

8. The method of claim 6 or 7, wherein the polymer solution comprises between about 70% and about 95% (by volume) of a solvent.

9. The method of claim 8, wherein the solvent is selected from a group consisting of acetone, chloroform, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone and tetrahydrofuran.

10. The method of claim 6 or 7, wherein the polymer solution comprises between about 5% and about 30% (by volume) of a polymeric material.