

FILTRATION MATERIAL FOR DESALINATION

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a filtration material for desalination, and in particular relates to a filtration material made of a water-swellaable polymer.

Description of the Related Art

[0002] Currently, filtration materials for desalination which are applied to sea water, industrial water and wastewater, have been developed by various sources all around the world. Conventionally, design issues concern the efficient treatment of salt water, the reduction of operating pressure, low energy consumption, and reduction in the cost of water treatment.

[0003] US Patent No.4828700 discloses a membrane made of cross-linked poly methyl methacrylate. The membrane performance has a 9.1 GFD flux, and a 97.9 % salt rejection, when tested under an operation pressure of 400 psi using 2500 ppm of salt water.

[0004] US Patent No.5755964 discloses a reverse osmosis (RO) membrane, wherein the RO membrane has good wetting property by using an amine compound to treat the surface of the RO membrane. The RO membrane performance has a 48 GFD flux, when tested under an operation pressure of 225 psi using 2000 ppm of salt water. The RO membrane exhibits high flux like nanofiltration material.

[0005] The filtration materials for desalination in prior art are made of nanoporous polymeric thin film. However, the nanoporous polymeric thin film must be operated under a high pressure. Alternatively, if the filtration materials are made of hydrophilic materials, the operation pressure may be decreased, which would thereby improve desalination

efficiency.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention provides a filtration material for desalination, comprising: a support layer, and a desalination layer formed on the support layer, wherein the desalination layer is a fiber composite membrane and comprises at least one water-swellaable polymer.

[0007] A detailed description is given in the following embodiments with reference to the accompanying drawings.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The following description is of the best-contemplated mode of carrying out the invention. This description is made for the purpose of illustrating the general principles of the invention and should not be taken in a limiting sense. The scope of the invention is best determined by reference to the appended claims.

[0009] The invention provides a filtration material for desalination, which comprises a support layer and a desalination layer formed on the support layer. The support layer is used to support the desalination layer. The desalination layer is a fiber composite membrane and comprises at least one water-swellaable polymer. The term “water-swellaable polymer” means that the polymer can swell itself by absorbing water. Although the polymer absorbs a lot of water, the structure of the polymer is not deformed. In some cases, the water-swellaable polymer is not a water soluble polymer and is made of hydrophilic monomers and hydrophobic monomers. Alternatively, the water-swellaable polymer is a water soluble polymer, and it maintains the swellaable property and reduces the hydrolysis property by an appropriate cross-linking reaction.

[0010] The support layer comprises one or more porous materials, wherein the porous

materials comprise cellulose ester, polysulfone, polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyetheretherketone (PEK), polyester (PET), polyimide (PI), chlorinated polyvinyl chloride (PVC) or styrene acrylonitrile (SAN). The support layer may be self-made or commercially available and may be in the form of non-woven, woven or open pores.

[0011] In one embodiment, the filtration material for desalination comprises two support layers in which a bottom layer is polyester (PET), and an upper layer is polyacrylonitrile (PAN) or polysulfone. The two support layers may be in the form of a non-woven or woven layer, and preferably non-woven layer.

[0012] The hydrophilic monomers of the water-swelling polymer comprise ionic monomers and non-ionic monomers.

[0013] The ionic monomers comprise cationic monomers and anionic monomers. The cationic monomers comprise acryloxyethyltrimethyl ammonium chloride, acryloxyethyltrimethyl benzyl ammonium chloride, methacryloxyethyltrimethyl ammonium chloride, methacryloxyethyltrimethyl p-toluenesulfonate, methacryloxyethyl dimethylbenzyl ammonium chloride, dimethylaminoethyl acrylate, t-butylaminoethyl methacrylate, vinyl imidazole or vinyl pyridine.

[0014] The anionic monomers comprise acrylic acid, methacrylic acid, itaconic acid, beta-carboxyethyl acrylate, maleic anhydride or sodium salt thereof. The examples of the anionic monomers are sodium acrylate, sodium 1-allyloxy-2-hydroxypropane sulfonate, ammonium allylpolyethoxy sulfate, sodium styrene sulfonate or 2-acrylamido-2-methyl propane sulfonic acid.

[0015] The non-ionic monomers comprise hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, acrylamide, N-hydroxyethyl acrylamide or polyvinylpyrrolidone.

[0016] The hydrophobic monomers comprise methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, t-butyl methacrylate, styrene or vinylidene fluoride. Additionally, although the monomers of acrylonitrile and methacrylonitrile are water soluble, the polymer made of these monomers are also used as the hydrophobic monomers.

[0017] In order to improve the mechanic strength of the fiber composite membrane, the water-swellaable polymer further reacts with a cross-linking agent to conduct a cross-linking reaction. The cross-linking agent may cross-linked to the hydrophilic or hydrophobic groups of the water-swellaable polymer (preferably to react with the hydrophilic groups) to reduce the solubility of the water-swellaable polymer. The cross-linking agent comprises acid anhydride, epoxy, isocyanate, aminoplast resins (the product of formaldehyde reacting with melamine, urea or guanamine), alkoxymethyl acrylamide, carbodiimide, aziridine or derivatives thereof.

[0018] In one embodiment, the acid anhydride is cross-linked to a hydroxyl group of the water-swellaable polymer. In another embodiment, the epoxy is cross-linked to a carboxyl group, a hydroxyl group, or an amine group of the water-swellaable polymer. In yet another embodiment, the isocyanate is cross-linked to a hydroxyl group of the water-swellaable polymer. In another embodiment, the aminoplast resins are cross-linked to a hydroxyl group, a carboxyl group or an amide group of the water-swellaable polymer. In one embodiment, the alkoxymethyl acrylamide is cross-linked to a hydroxyl group of the water-swellaable polymer. In yet another embodiment, the carbodiimide or aziridine is cross-linked to a carboxyl group of the water-swellaable polymer.

[0019] In addition to the chemical cross-linking reaction, the cross-linking reaction further comprises an ionic cross-linking reaction. For example, a multi-chlorinated hydrocarbon is cross-linked to an amine group of the water-swellaable polymer to form a

quaternary ammonium salt. In one embodiment, 1,6-dichlorohexane is cross-linked to an amine group of the water-swellaable polymer to form a quaternary ammonium salt to complete a quaternization reaction for ionic crosslinking.

[0020] Furthermore, the hydrophilic group of the water-swellaable polymer may react with crosslinkable monomers, such as N-isobutoxymethyl acrylamide.

[0021] Moreover, the water-swellaable polymer may be made of a modified polymer, such as polyvinyl alcohol, carboxymethyl cellulose or hydroxyethyl cellulose. The polyvinyl alcohol is the hydrolysis product of the polyvinylacetate, and the hydroxyethyl cellulose is an addition reaction product by reacting ethylene oxide with cellulose.

[0022] Additionally, the fiber composite membrane is in the form of a fiber with a binder, and the fiber is made from water-swellaable polymer by spinning techniques, such as solution spinning or electrospinning. Then, the binder is filled in the fiber by coating or dipping. Finally, after a roller or plate process, a dense fiber composite membrane is obtained.

[0023] The binder may be a water-swellaable polymer or other polymers, other polymers are such as polyvinyl alcohol (PVA), polystyrene (PS), polyacrylamides, polymethacrylamides, polymethacrylates, polyacrylates, polyester, hydroxyethyl cellulosic or hydroxypropyl cellulose.

[0024] The function of the binder is to improve the mechanic strength of the filter materials and narrow the holes in the surface of desalination layer.

[0025] In order to reduce solubility of the fiber composite membrane and enhance the mechanical strength of fiber composite membrane, an additional cross-linking agent is added into the binder. For example, methylated melamine-formaldehyde resin (such as hexamethoxymethylmelamine) is added into the binder, and it is cross-linked to a hydroxyl group of the fiber composite membrane to change the solubility of the fiber composite

membrane.

[0026] In one embodiment, the fiber is made from the water-swellaable polymer by electrospinning. Then, the binder of polyacrylonitrile (PAN) is added into the fiber to form the fiber composite membrane.

[0027] In another embodiment, the fiber is made from polyacrylonitrile (PAN) by electrospinning. Then, the binder of water-swellaable polymer is added into the fiber to form the fiber composite membrane.

[0028] In a preferably embodiment, the fiber is made from the water-swellaable polymer by electrospinning. Then, the binder of water-swellaable polymer is added into the fiber to form the fiber composite membrane.

[0029] The fiber of the fiber composite membrane of the invention comprises a microfiber or nanofiber, wherein the microfiber has a diameter of about 1-30 μm , preferably 1-15 μm , and the nanofiber has a diameter of about 10-1000 nm, preferably 50-500 nm.

[0030] The conventional reverse osmosis (RO) membranes have smaller pores (smaller than 1 nm). Thus, the membranes must be operated under a pressure which is larger than about 500 psi, even 1000 psi. The main advantage of the invention is that the filtration material of the invention can exhibit high flux as with the conventional RO membrane, but may be operated under a lower pressure environment. Flux of the filtration material of the invention is 18 $\text{L}/\text{m}^2/\text{hr}$, and salt rejection is 60 %-90 %, when tested under an operation pressure smaller than 10 psi.

[0031] Compared with prior art, the open pores of the fiber composite membrane of the invention may be used as an effective desalination membrane, thus the filtration material of the invention may be operated under a lower pressure environment. Note that the filtration material of the invention is only made by one support layer with one desalination layer for

desalination effect. The filtration material may be additionally combined with other conventional permeable, semi-permeable membranes or other polymer films according to actual application.

[0032] Because the fiber composite membrane has the porous properties, the filtration material of the invention has a desalination effect, and the filtration material still has high flux even if operated under lower pressure. The filtration material of the invention may be used in a desalination process, wastewater treatment, ultrapure water treatment, water softening or heavy metals recovery.

[0033] 【Example】

[0034] Comparative Example 1

[0035] The filtration material of **Comparative Example 1** is made by two support layers. A bottom layer is polyester (PET) non-woven (purchased from HO YU TEXTILE CO., LTD) and an upper layer is polyacrylonitrile (PAN) (purchased from TONGHWA synthetic fiber CO. Ltd., molar weight of about 150,000~300,000).

[0036] Comparative Example 2

[0037] The support layer of **Comparative Example 1** was used as the support layer of **Example 2**.

[0038] The desalination layer of **Comparative Example 2** was fabricated as following. 30 g of polyacrylonitrile (PAN) was dissolved in 200 g of N, N-dimethyl-acetamide (DMAc) to provide a spinning solution. The nanofiber material was obtained by electrospinning with an applied voltage of 39 KV, spray amount of 1000 $\mu\text{L}/\text{min}$, a 25 cm distance between the collector and spinneret, and air pressure of 2.8 kg/cm^3 . A nanofiber material with a diameter of 280 nm-380 nm and weight of 30-60 g/m^2 was obtained.

[0039] 3 g of polystyrene (PS) (purchased from Aldrich, used as binder) was dissolved in 27 g p-xylene to form a mixture. Next, the mixture was coated on the above nanofiber

material at 70°C for 1 hours to form the fiber composite membrane.

[0040] Example 1 fabrication of the water-swellaable polymer

[0041] 10 g of sodium styrenesulfate, 40 g of 4-vinyl pyridine, 7 g of styrene, 50 g of deionized water and 50 g of isopropanol (IPA) were dissolved in a reaction flask, and stirred under N₂ atmosphere at 70°C. A solution containing 0.2 g of potassium persulfate (KPS) in 10 mL of deionized water was slowly added into the reaction flask, and kept for 3 hours. The mixture was purified to obtain 50.1 g of the water-swellaable polymer (88 %).

[0042] Example 2 fabrication of nanofiber materials

[0043] 36 g of the polymer of **Example 1** was dissolved in 200 g of N, N-dimethylacetamide (DMAc) to provide a spinning solution. The nanofiber material was obtained by electrospinning with an applied voltage of 39 KV, spray amount of 1200 µL/min, a 20 cm distance between the collector and spinneret, and air pressure of 5 kg/cm³. A nanofiber material with a diameter of 70 nm-120 nm and weight of 60-94 g/m² was obtained.

[0044] Example 3 fabrication of nanofiber composite materials

[0045] 30 g of polyacrylonitrile (PAN) was dissolved in 200 g of N, N-dimethylacetamide (DMAc) to provide a spinning solution. The nanofiber material was obtained by electrospinning with an applied voltage of 39 KV, spray amount of 1000 µL/min, a 25 cm distance between the collector and spinneret, and air pressure of 2.8 kg/cm³. A nanofiber material with a diameter of 280 nm-380 nm and weight of 30-60 g/m² was obtained.

[0046] Example 4

[0047] The support layer of **Comparative Example 1** was used as the support layer of **Example 4**.

[0048] The desalination layer of **Example 4** was fabricated as following. 3 g of **Example 1** (used as binder) was dissolved in 27 g alcohol, and then 2.6 g of 1,6-

dichlorohexane (used as cross-linking agent) was added into the alcohol to form a mixture. Next, the mixture was coated on the nanofiber material of **Example 2** at 70°C for 4 hours to form the fiber composite membrane.

[0049] Example 5

[0050] The support layer of **Comparative Example 1** was used as the support layer of **Example 5**.

[0051] The desalination layer of **Example 5** was fabricated as following. 0.6 g of **Example 1** (used as binder) was dissolved in 29.4 g alcohol, and then 0.42 g of 1,6-dichlorohexane (used as cross-linking agent) was added into the alcohol to form a mixture. Next, the mixture was coated on the nanofiber material of **Example 3** at 70°C for 4 hours to form the fiber composite membrane.

[0052] Example 6

[0053] The support layer of **Comparative Example 1** was used as the support layer of **Example 6**.

[0054] The desalination layer of **Example 6** was fabricated as following. 3 g of commercially available polystyrene (PS) (used as binder) was dissolved in 27 g p-xylene to form a mixture. Next, the mixture was coated on the nanofiber material of **Example 2** at 70 °C for 1 hour to form the fiber composite membrane.

[0055] Example 7

[0056] The support layer of **Comparative Example 1** was used as the support layer of **Example 7**.

[0057] The desalination layer of **Example 7** was fabricated as following. 3 g of **Example 1** (used as binder) was dissolved in 27 g alcohol, and then 2.1 g of 1,6-dichlorohexane (used as cross-linking agent) was added into the alcohol to form a mixture.

Next, the mixture was coated on the commercial available polypropylene (PP) nanofiber material at 70°C for 4 hours to form the fiber composite membrane.

[0058] Example 8

[0059] The support layer of **Comparative Example 1** was used as the support layer of **Example 8**.

[0060] The desalination layer of **Example 8** was fabricated as following. 10 g of polyvinyl alcohol (PVA) (purchased from ChangChun Group) (used as binder) was dissolved in 90 g water, and then 0.01 g of maleic anhydride (MA) (used as cross-linking agent) was added into the water to form a mixture. Next, the mixture was coated on the nanofiber material of **Example 3** at 70°C for 4 hours to form the fiber composite membrane.

[0061] The desalination efficiency of **Comparative Example 1-2** and **Example 4-8** are shown in Table 1. As shown in Table 1, the filtration material made by the water-swallowable polymer of the invention had a good desalination effect, with desalination efficiency of about 50-95%.

[0062] Table 1

Example	fiber	binder	Desalination efficiency (%)
Comparative Example 1	none (only support layer)		0 %
Comparative Example 1	PAN (commercial available)	PS (commercial available)	54.63 %
Example 4	The polymer of	The polymer of	96.7 %

	Example 1	Example 1	
Example 5	PAN (commercial available)	The polymer of Example 1	87.58 %
Example 6	The polymer of Example 1	PS (commercial available)	82.50%
Example 7	PP (commercial available)	The polymer of Example 1	64.28 %
Example 8	PAN (commercial available)	PVA (commercial available)	65.04 %

[0063] While the invention has been described by way of example and in terms of the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, it is intended to cover various modifications and similar arrangements (as would be apparent to those skilled in the art). Therefore, the scope of the appended claims should be accorded the broadest interpretation so as to encompass all such modifications and similar arrangements.

What is claimed is:

1. A filtration material for desalination, comprising:

a support layer; and

a desalination layer formed on the support layer, wherein the desalination layer is a fiber composite membrane and comprises at least one water-swellaable polymer copolymerized of styrene sulfate, 4-vinyl pyridine, and styrene.

2. The filtration material as claimed in claim 1, wherein the support layer comprises one or more porous materials.

3. The filtration material as claimed in claim 2, wherein the porous materials comprise cellulose ester, polysulfone, polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyetheretherketone (PEK), polyester (PET), polyimide (PI), chlorinated polyvinyl chloride (PVC) or styrene acrylonitrile (SAN).

4. The filtration material as claimed in claim 1, wherein the fiber composite membrane is in the form of a fiber with a binder, and the fiber comprises microfiber or nanofiber.

5. The filtration material as claimed in claim 1, wherein the water-swellaable polymer reacts with a cross-linking agent to conduct a cross-linking reaction.

6. The filtration material as claimed in claim 5, wherein the cross-linking agent comprises acid anhydride, epoxy, isocyanate, aminoplast resins, alkoxymethyl acrylamide, carbodiimide, aziridine or derivatives thereof.

7. The filtration material as claimed in claim 6, wherein the cross-linking agent comprises epoxy and the epoxy is cross-linked to a hydroxyl group or an amine group of the water-swellaable polymer.

8. The filtration material as claimed in claim 6, wherein the cross-linking agent comprises isocyanate and the isocyanate is cross-linked to a hydroxyl group of the water-swellaable polymer.

9. The filtration material as claimed in claim 6, wherein the cross-linking agent comprises aminoplast resins and the aminoplast resins are cross-linked to a hydroxyl group of the water-swellaable polymer.

10. The filtration material as claimed in claim 6, wherein the cross-linking agent comprises acid anhydride and the acid anhydride is cross-linked to a hydroxyl group of the water-swellaable polymer.

11. The filtration material as claimed in claim 6, wherein the cross-linking agent comprises alkoxymethyl acrylamide and the alkoxymethyl acrylamide is cross-linked to a hydroxyl group of the water-swellaable polymer.

12. The filtration material as claimed in claim 5, wherein the cross-linking reaction comprises an ionic cross-linking reaction.

13. The filtration material as claimed in claim 5, wherein a multi-chlorinated hydrocarbon is cross-linked to an amine group of the water-swellaable polymer to form a quaternary ammonium salt.