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(54) Title: ASYMMETRICALLY POROUS ION EXCHANGE MEMBRANES AND THEIR METHOD OF MANUFACTURE

(57) Abstract: The invention relates to a membrane and method for its manufacture, the method including the steps of (1) providing of an ultrafiltration membrane, and (2) modification of the resultant ultrafiltration membrane to provide an asymmetric porous ion exchange membrane. The modification of the ultrafiltration membrane is typically carried out by (i) exposing said ultrafiltration membrane to a first functional reagent to provide a cross-linked ultrafiltration membrane, and then (ii) exposing said cross-linked ultrafiltration membrane to a second functional reagent to introduce positive charged groups to produce an anion exchange membrane.



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ASYMMETRICALLY POROUS ION EXCHANGE MEMBRANES AND THEIR METHOD OF MANUFACTURE

FIELD OF INVENTION

[0001] The present invention relates to the field of membrane technology.

[0002] In one form, the invention relates to a new asymmetrically porous ion exchange membrane and a method of manufacture thereof.

[0003] In one particular aspect the present invention is suitable for use as a diffusion dialysis membrane.

[0004] It will be convenient to hereinafter describe the invention in relation to industrial diffusion dialysis membranes, however it should be appreciated that the present invention is not limited to that use only, and can for example, also be used in other applications, such as sodium salicylate (charged medicine) recovery in medical separation.

BACKGROUND ART

[0005] It is to be appreciated that any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the present invention. Further, the discussion throughout this specification comes about due to the realisation of the inventor and/or the identification of certain related art problems by the inventor. Moreover, any discussion of material such as documents, devices, acts or knowledge in this specification is included to explain the context of the invention in terms of the inventor's knowledge and experience and, accordingly, any such discussion should not be taken as an admission that any of the material forms part of the prior art base or the common general knowledge in the relevant art in Australia, or elsewhere, on or before the priority date of the disclosure and claims herein.

[0006] Large amount of acidic or basic waste solutions produced from industrial production cause serious environmental problems and resources waste. The common

acid/base waste treatments of the prior art suffer from high energy consumption and increase pollution by generating salt by-products. Acid/base recovery via diffusion dialysis employing ion exchange membranes has been used for many years due to its operational simplicity, compatibility with either small or large plating plants and economic advantages in terms of capital investment and operating costs.

[0007] However, the processing capacity and efficiency of diffusion dialysis systems are still quite low (e.g., $11.3 \text{ L.m}^{-2}.\text{d}^{-1}$ for the commercial DF-120 membrane with acid recovery of 85-90%), thus requiring large membrane areas for industrial applications. This drawback is due to the low ion permeation of the ion exchange membranes used, which are generally prepared by direct evaporation of quaternized polymer solution.

[0008] Numerous efforts have been made in the past to improve the diffusion dialysis performance of the dense ion exchange membranes by modifying their structure. However, the membrane microstructure of the prior art remains of dense structure and improvement is thus limited. There is therefore an ongoing need to create improved structures with concomitantly improved performance.

SUMMARY OF INVENTION

[0009] An object of the present invention is to provide membranes having improved diffusion dialysis performance.

[0010] Another object of the present invention is to create improved membrane structures or at least improve existing membrane structures.

[0011] A further object of the present invention is to alleviate at least one disadvantage associated with the related art.

[0012] It is an object of the embodiments described herein to overcome or alleviate at least one of the above noted drawbacks of related art systems or to at least provide a useful alternative to related art systems.

[0013] In a first aspect of embodiments described herein there is provided a method for manufacture of a membrane comprising the step of direct conversion of an ultrafiltration membrane having an asymmetric microstructure after modification such as by the steps of cross-linking and charging treatment.

[0014] In a second aspect of embodiments described herein there is provided a method for manufacture of a membrane comprising the steps of;

- (1) provision of an ultrafiltration membrane, and
- (2) modification of the resultant ultrafiltration membrane to provide an asymmetrically porous ion exchange membrane.

[0015] In contrast with the dense ion exchange membranes of the prior art which are typically dense and of symmetric structure, the asymmetrically porous membranes produced by the method of the present invention have a different micro-structure and a different ion transfer rate through the membrane matrix. Typically the membranes of the present invention have an asymmetrical microstructure with a dense top surface without observable pores (that is, pores typically having a diameter of less than 0.8 nm), a thin nanoporous active layer, macroporous supporting layer with asymmetrically porous channels within the cross section and a macroporous bottom surface. Without wishing to be bound by theory it is believed that blocking the nanopores of the skin layer is responsible for the high acid/base permeability.

[0016] The ultrafiltration membrane of step (1) may be pre-manufactured according to any convenient means and may comprise at least one halogen methylated polymer. Alternatively, the ultrafiltration membrane of step (1) may be prepared from a starting polymer can be selected from halogen methylated polymers such as chloromethylated polysulfone (PS-Cl), chloromethylated polyethersulfone (PES-Cl), chloromethylated poly(ether ketone) (PEK-Cl), chloromethylated poly (ether ether ketone) (PEEK-Cl), chloromethylated poly (phthalazinone ether sulfone ketone) (PPESK-Cl) and bromomethylated poly (phenylene oxide) (BPPO).

[0017] Typically, step (2) comprises modification of the ultrafiltration membrane using a one-step or two-step method to produce a porous ion exchange membrane.

[0018] In a third aspect of embodiments described herein there is provided a method for manufacture of a membrane comprising the steps of;

- (1)(i) forming a solution comprising 10 to 40 wt% of one or more halogen methylated polymers,
- (1)(ii) casting the solution to a thickness of 10 to 500 micron, and
- (1)(iii) subjecting the cast solution to a coagulation bath to form an ultrafiltration membrane, and
- (2) modification of the resultant ultrafiltration membrane by exposing it to at least one functional reagent to provide a porous ion exchange membrane.

[0019] Step (2) may comprise one or two sub-steps. In a fourth aspect of embodiments described herein there is provided a method for manufacture of a membrane comprising the steps of;

- (1) preparation of an ultrafiltration membrane using a polymer, and
- (2) modification of the resultant ultrafiltration membrane to provide a porous ion exchange membrane by;
 - exposing said ultrafiltration membrane to a bis-functional reagent, or
 - exposing said ultrafiltration membrane to (i) a first functional reagent to provide a cross-linked ultrafiltration membrane, and then (ii) a second functional reagent to introduce positive charged groups into the membranes to produce an anion exchange membrane, or

- exposing said ultrafiltration membrane to (i) a first functional reagent to cross-link the ultrafiltration membrane and then (ii) a second functional reagent to introduce negatively charged groups into the membranes to produce a cation exchange membrane.

[0020] For the one step method for anion exchange membrane preparation, the bis-functional reagent is selected from the group comprising imidazoles and amines containing at least two amine groups and at least one of them should be a tertiary amine group, such as N,N,N',N'--tetramethylethylenediamine, N,N,N',N'--tetramethyl-1,3-propanediamine, N,N,N',N'--tetramethyl-1,4-butanediamine, N,N,N',N'--tetramethyl-1,6-hexanediamine, N,N-dimethylethylenediamine, 3-(dimethylamino)-1-propylamine, 3,3'-iminobis(N,N-dimethylpropylamine), and 1,4-diazabicyclo[2.2.2]octane.

[0021] Typically the first functional reagent is selected from amines containing at least two amine groups, such as ethylenediamine, hexamethylenediamine, diethylenetriamine, diethylenetriamine, pentaethylenehexamine, poly(ethyleneimine) and poly(ethylene glycol) bis(amine), or mixtures thereof.

[0022] Typically the second functional reagents for anion exchange membrane preparation is selected from the molecules that can be transferred to positively charged compound after reaction with halomethyl such as N-substituted imidazole, tris(3,5-dimethylphenyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, tris(2,4,6-trimethylphenyl)phosphine, tris(3,5-dimethylphenyl)phosphine, or amines molecules with a tertiary amine group such as trimethylamine, tripropylamine and trihexylamine or mixtures thereof.

[0023] Typically the second functional reagents for cation exchange membrane preparation is selected from the molecules that can and introduce negatively charged groups after reaction with membrane substrate such as concentrated sulfuric acid, chlorosulfonic acid, potassium 4-(1H-indol-3-yl)butanoate, 3-Indoleacetic acid, Indole-3-butyric acid.

[0024] For the one step or two step method the first and second functional reagents can be used neat or diluted with solvent(s) depending on the nature of the reagents.

[0025] In another aspect of embodiments described herein there is provided an ultrafiltration membrane manufactured according to the method of the present invention comprises,

a dense top surface without observable pores,

a thin nanoporous active layer,

a macroporous supporting layer with asymmetrically porous channels within the cross section, and

a macroporous bottom surface.

[0026] In yet a further aspect of embodiments described herein there is provided a membrane manufactured according to the method of the present invention, the membrane has an asymmetrical microstructure with (i) a dense top surface, (ii) a thin nanoporous active layer, (iii) a macroporous supporting layer with asymmetrically porous channels, and (iv) a macroporous bottom surface.

[0027] Other aspects and preferred forms are disclosed in the specification and/or defined in the appended claims, forming a part of the description of the invention.

[0028] In essence, embodiments of the present invention stem from the realization that particular features incorporated into a membrane structure can significantly improve diffusion dialysis performance. In particular the realisation is based at least in part in the realisation that blocking or eliminating nanopores in the skin layer of an ultrafiltration membrane can increase the acid/base permeability and the separation factor.

[0029] Advantages provided by the present invention comprise the following:

- the method for manufacture of the membranes is simple and effective,
- the membranes have potential to improve process capacity and efficiency of diffusion dialysis, such as for rapid acid/base recovery,

- the membranes have ultrahigh acid/base permeability and separation factor,
- the membranes have low effective thickness and high porosity.

[0030] Further scope of applicability of embodiments of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure herein will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] Further disclosure, objects, advantages and aspects of preferred and other embodiments of the present application may be better understood by those skilled in the relevant art by reference to the following description of embodiments taken in conjunction with the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the disclosure herein, and in which:

FIG. 1 is a schematic representation of the cross-section morphologies and ion transfer mechanisms of (a) dense anion exchange membranes and (b) asymmetrically porous anion exchange membranes (where H^+ indicates protons, A^- indicates anions, and M^+ indicates metal ions);

FIG. 2 is a schematic representation of the cross-section morphologies and ion transfer mechanisms of (a) dense cation exchange membranes and (b) asymmetrically porous cation exchange membranes (where OH^- indicates hydroxide ions, C^+ indicates cations and A^- indicates anions; nanochannel (2); wall (4); water (6));

FIG. 3 is a schematic representation of the steps involved in the method of manufacture of a porous anion/cation exchange membrane according to the present invention. The schematic shows:

1 – addition of organic solvent to a polymer to form a polymer solution	15 – modification of the ultrafiltration membrane by addition of a bis-functional reagent
3 – applying a micrometer film applicator	17 – formation of a porous anion exchange membrane
5 – applying to a substrate	19 – addition of a first functional reagent to cause cross-linking
7 – forming a casting solution	21 – addition of an alternative second functional reagent to introduce positively charged groups
9 – subjecting the casting solution of af a coagulation bath	23 – formation of a cross-linked ultrafiltration membrane
11 – formation of an ultrafiltration membrane	25 – formation of a porous anion exchange membrane
13 – formation of halogen methylated polymers	27 – addition of another second functional reagent to introduce negatively charged groups
	29 – formation of a porous cation exchange membrane

FIG. 4 is a representation of a high-resolution XPS spectra of N1s region of BPPO (30) and TPPO (32) membranes;

FIG. 5 comprises SEM images of a porous TPPO ultrafiltration membrane depicting (a) the top surface, (b) the bottom surface, (c) the cross section of the overall membrane (d) the cross section of the skin layer with a thickness of sub-1 μ m;

FIG. 6 is a representation of high-resolution XPS spectra of N1s region of BPPO (34), BBPPO (36) and BTPPO (38) membranes;

FIG. 7 comprises SEM images of BTPPO ultrafiltration membrane depicting (a) the top surface, (b) the bottom surface, (c) the cross section of the overall membrane (d) the cross section of the skin layer with a thickness of sub-1 μ m;

FIG. 8 illustrates the acid dialysis coefficient and separation factor of TPPO (■), BTPPO (●), commercially available DF120 membrane (▲) and some other membranes of the prior art (▼).

DETAILED DESCRIPTION

[0032] In contradistinction to dense membranes, ultrafiltration membranes have a thin nanoporous skin layer with a thickness of sub-micrometer and a thick and macroporous supporting layer. Typical ultrathin membranes of the prior art are described by Guillen et al., in *Preparation and Characterization of Membranes Formed by Nonsolvent Induced Phase Separation: A Review*, Industrial & Engineering Chemistry Research, 2011, 50(7), p. 3798-3817. High acid/base permeability can be expected after the nanopores of the skin layer have been blocked.

[0033] Typically, the transport of small molecules across a dense or nonporous polymer membrane follows a solution-diffusion mechanism involving sorption of solutes into the membrane, diffusion across the membrane and desorption of solutes out of the membrane. Among these process, diffusion across the membrane under a 'hopping' mechanism or 'vehicular' mechanism is the most important and largely dependent on the free volume of the polymer.

[0034] FIG. 1 shows the cross-section morphologies of (a) a dense anion exchange membrane and (b) an asymmetrically porous anion exchange membrane for diffusion dialysis and the proton transfer mechanisms through them.

[0035] For dense anion exchange membrane, ion transfer rate is low because of the less free volume and the high thickness (dozens to hundreds μm). For asymmetrically porous anion exchange membranes, protons may firstly transport through the thin skin layer (typically $<1 \mu\text{m}$ thick) via nano-channels. The transport rate should be higher than dense membrane with the same thickness because of the larger free volume. Afterwards, ion transport rate in the supporting layer should be accelerated because of the abundant water absorbed in the finger-linked macro-channels.

[0036] The proton diffusivity across the whole asymmetrically porous anion exchange membrane is significantly higher than the ion diffusivity across the dense anion exchange membrane. The difference in the micro-structure between the dense and ultrafiltration membrane results in the difference in ion transfer rate in the membrane matrix. Moreover, since ultrafiltration membranes can be conveniently prepared via a phase inversion technique (such as the technique disclosed in Lin et al, J. Membrane Sci., 2015, 482(0): p. 67-75) the conversion of ultrafiltration membranes is a simple and effective method for the large-scale production of diffusion dialysis membranes with high-performance.

[0037] FIG. 2 shows the cross-section morphologies of (a) a dense anion exchange membrane and (b) an asymmetrically porous cation exchange membrane for diffusion dialysis and the hydroxide transfer mechanisms through them.

[0038] Same to the mechanism described for the asymmetrically porous anion exchange membrane, the hydroxide diffusivity across the whole asymmetrically porous cation exchange membrane is significantly higher than the hydroxide diffusivity across the dense cation exchange membrane. Therefore high base permeability can be obtained.

Manufacture of the Ultrafiltration Membrane

[0039] Step (1) of the method of manufacture according to the present invention comprises preparation of an ultrafiltration membrane using a polymer. As mentioned previously the polymer can be selected from many halogen methylated polymers such as chloromethylated polysulfone (PS-Cl), chloromethylated polyethersulfone (PES-Cl), chloromethylated poly(ether ketone) (PEK-Cl), chloromethylated poly (ether ether ketone) (PEEK-Cl), chloromethylated poly (phthalazinone ether sulfone ketone) (PPESK-Cl) and bromomethylated poly (phenylene oxide) (BPPO).

[0040] The polymer is typically dissolved. The organic solvent used for dissolving the polymer can be a single solvent or a mixture of solvents. In a preferred embodiment the solvent is chosen from the group comprising N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAC), or mixtures thereof. The choice

of solvent(s) will depend on the types of polymers used in the membrane fabrication, and desired microstructure of the final membranes.

[0041] The halogen methylated polymer is dissolved in organic solvent to form a casting solution. Typically the polymer concentration is 10-40wt%.

[0042] The solution is then cast with a typical thickness of 100-500 μm . The casting may for example be carried out using a micrometer film applicator on a clean flat substrate (such as a glass plate). The ultrafiltration membrane may be produced in a coagulation bath filled with water or other solvents, followed by washing thoroughly in deionized water. The resulting membrane is soaked in deionized water for future modification.

[0043] The method of manufacturing a membrane according to the present invention is described in the following non-limiting Examples. FIG. 3 is a schematic representation of the steps involved in the method of manufacture of an asymmetrically porous anion exchange membrane according to the present invention;

Example 1 – Manufacture using a Single Modification Step for anion exchange membrane preparation

[0044] Commercial bromomethylated poly (phenylene oxide) (BPPO) was used for preparation of an ultrafiltration membrane according to the present invention. The BPPO was dissolved in N-methyl-2-pyrrolidone to form a casting solution, which was cast onto a glass by a micrometer film applicator and then immersed into distilled water as coagulation bath to get the ultrafiltration membrane with benzyl bromide groups ($-\text{CH}_2\text{Br}$) groups. The ultrafiltration membrane was then modified via one-step method by soaking in N,N,N',N'-tetramethylethylenediamine (TEMED) aqueous solution to get the final porous TPPO anion exchange membrane.

[0045] The concentration and thickness of the casting solution, the concentration of TEMED as the bis-functional reagent and the soaking temperature and time of ultrafiltration membrane in the TEMED solution can be varied to fabricate the

asymmetrically porous anion exchange membranes with different diffusion dialysis properties.

[0046] For example, when the concentration and thickness of the casting solution is 30wt% and 250 μm , respectively, the concentration of the bis-functional reagent is 1 mol.L^{-1} , the soaking temperature and time are 30°C and 4 hours, respectively, the resulting TPPO membrane has an acid dialysis coefficient of 0.043 m.h^{-1} and separation factor of 73.8 when applied to recovery HCl from the mixture of HCl and FeCl_2 aqueous solution as the model acidic waste solution, which are 4.1 times and 3.0 times greater than the commercial DF-120 membrane under identical testing condition.

[0047] FIG. 6 shows high-resolution XPS spectra of N1s region of BPPO and TPPO membranes. The newly formed peak at 402.4eV from BPPO to TPPO membrane confirms the successful introduction of quaternary ammonium (positively charged) groups into TPPO membrane.

[0048] As shown in FIG. 5, after simultaneously crosslinking and quaternization by TEMED, the final TPPO membrane exhibits a porous structure at the supporting layer with a dense active layer (as the effective layer) with a thickness of sub-1 μm , and no observable pores at both of the top and bottom surfaces can be found. The porous micro-structure and the extremely low thickness would endow TPPO membranes with high proton permeability and hence improve the acid recovery rate when TPPO membranes were applied to recovery acid via diffusion dialysis.

Example 2 – Manufacture Using a Two Step Modification for anion exchange membrane preparation

[0049] Commercial bromomethylated poly (phenylene oxide) (BPPO) was used as the starting for ultrafiltration membrane preparation. It was dissolved in N-methyl-2-pyrrolidone to form a casting solution with the concentration of 30 wt%, which was cast onto a glass by a micrometer film applicator whose gap was set as 250 μm and then immersed into distilled water to get the ultrafiltration membrane with benzyl bromide groups ($-\text{CH}_2\text{Br}$) groups. The ultrafiltration membrane was then modified via two-steps method by soaking in butanediamine (BTDA) aqueous solution to get the cross-linked

BBPPO membrane and then soaking in trimethylamine (TMA) aqueous solution in turn to get the final porous BTPPO anion exchange membrane.

[0050] The concentration of BTDA and TMA aqueous solution as the first and second functional reagent, respectively, and the soaking temperature and time of ultrafiltration membrane in the BTDA and TMA solution respectively can be varied to fabricate the final porous membranes with different diffusion dialysis properties. For example, when the concentration of the BTDA solution was 1 mol.L^{-1} , the soaking temperature and time were 40°C and 1 hour, the concentration of the TMA solution was 1 mol.L^{-1} , the soaking temperature and time were 60°C and 6 hours. The resultant BTPPO ultrafiltration membrane had an acid dialysis coefficient of 0.062 m h^{-1} and separation factor of 30.4 when applied to recovery HCl from the mixture of HCl and FeCl_2 aqueous solution, which are 6.3 times and 0.6 times greater than the commercial DF-120 membrane of the prior art under identical testing condition.

[0051] Similar to Example 1 described above, the newly formed peak at 402.4ev for BTPPO membrane (as shown in FIG. 6) confirms the successful introduction of quaternary ammonium (positively charged) groups into BTPPO membrane.

[0052] As shown in FIG. 7, the BTPPO membrane after treatment by BTDA and TMA also shows a porous structure at the supporting layer with a dense active layer (as the effective layer), having a thickness less than $1 \mu\text{m}$. Moreover, no obvious pores at the top and bottom surfaces can be observed.

[0053] The acid dialysis coefficient and separation factor of TPPO and BTPPO are plotted in FIG. 8 in comparison with prior art membranes such as the commercial DF-120 membrane and some recently reported anion exchange membranes used in diffusion dialysis. In FIG. 8, the acid dialysis coefficients and separation factor of all the membranes were determined by the same testing method using a solution comprising a mixture of HCl and FeCl_2 . There is a trade-off between the acid dialysis coefficient and separation factor.

[0054] As clearly shown in FIG. 8, TPPO and BTPPO membranes show extraordinarily good diffusion dialysis performance including high acid dialysis coefficient and separation factor as compared with all other membranes.

Example 3 – Manufacture Using a Two Step Modification for cation exchange membrane preparation

[0055] Commercial bromomethylated poly (phenylene oxide) (BPPO) was used as the starting material for ultrafiltration membrane preparation. It was dissolved in N-methyl-2-pyrrolidone to form a casting solution with the concentration of 30 wt%, which was cast onto a glass by a micrometer film applicator whose gap was set as 250 μm and then immersed into distilled water to get the ultrafiltration membrane with benzyl bromide groups ($-\text{CH}_2\text{Br}$) groups. The ultrafiltration membrane was then modified via two-steps method by soaking in butanediamine (BTDA) aqueous solution to get the cross-linked BBPPO membrane and then soaking in chlorosulfonic acid aqueous solution in turn to get the final porous cation exchange membrane.

[0056] The concentration of BTDA and chlorosulfonic acid aqueous solution as the first and second functional reagent, respectively, and the soaking temperature and time of ultrafiltration membrane in the BTDA and chlorosulfonic acid solution respectively can be varied to fabricate the final porous membranes with different diffusion dialysis properties. The resultant asymmetrically porous cation membranes show good diffusion dialysis for base recovery and mechanical properties.

[0057] While this invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification(s). This application is intended to cover any variations uses or adaptations of the invention following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth.

[0058] As the present invention may be embodied in several forms without departing from the spirit of the essential characteristics of the invention, it should be understood

that the above described embodiments are not to limit the present invention unless otherwise specified, but rather should be construed broadly within the spirit and scope of the invention as defined in the appended claims. The described embodiments are to be considered in all respects as illustrative only and not restrictive.

[0059] Various modifications and equivalent arrangements are intended to be included within the spirit and scope of the invention and appended claims. Therefore, the specific embodiments are to be understood to be illustrative of the many ways in which the principles of the present invention may be practiced. In the following claims, means-plus-function clauses are intended to cover structures as performing the defined function and not only structural equivalents, but also equivalent structures.

[0060] “Comprises/comprising” and “includes/including” when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, ‘includes’, ‘including’ and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

CLAIMS

1. A method for manufacture of a membrane comprising the steps of
 - (1) provision of an ultrafiltration membrane, and
 - (2) modification of the resultant ultrafiltration membrane to provide an asymmetric porous ion exchange membrane.
2. A method according to claim 1 wherein the ultrafiltration membrane comprises at least one halogen methylated polymer.
3. A method according to claim 1 wherein the asymmetric porous ion exchange membrane comprises,
 - a dense top surface without observable pores,
 - a thin nanoporous active layer,
 - a macroporous supporting layer with asymmetrically porous channels within the cross section, and
 - a macroporous bottom surface
4. A method according to claim 1 wherein step (1) comprises the steps of;
 - (1)(i) forming a solution comprising 10 to 40 wt% of one or more halogen methylated polymers,
 - (1)(ii) casting the solution to a thickness of 10 to 500 micron,
 - and
 - (1)(iii) subjecting the cast solution to a coagulation bath to form an ultrafiltration membrane.

5. A method according to claim 1 wherein step (2) comprises the sub-step of exposing the ultrafiltration membrane of step (1) to a bis-functional reagent, preferably an imidazoles or amine containing at least two amine groups.
6. A method according to claim 1 wherein step (2) comprises the sub-steps of,
- (i) exposing said ultrafiltration membrane to a first functional reagent to provide a cross-linked ultrafiltration membrane, and then
 - (ii) exposing said cross-lined ultrafiltration membrane to a second functional reagent to introduce positive charged groups to produce an anion exchange membrane.
7. A method according to claim 6 wherein the second functional reagent is selected from molecules that can be transferred to positively charged compound after reaction with halomethyl, preferably N-substituted imidazole, tris(3,5-dimethylphenyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, tris(2,4,6-trimethylphenyl)phosphine, tris(3,5-dimethylphenyl)phosphine, or amines molecules with a tertiary amine group such as trimethylamine, tripropylamine and trihexylamine or mixtures thereof.
8. A method according to claim 1 wherein step (2) comprises the sub-steps of;
- (i) exposing said ultrafiltration membrane to a first functional reagent to provide a cross-linked ultrafiltration membrane, and then
 - (ii) exposing said cross-lined ultrafiltration membrane to a second functional reagent to introduce negatively charged groups to produce a cation exchange membrane.
9. A method according to claim 8 wherein the second functional reagent is selected from molecules that can and introduce negatively charged groups after reaction with membrane preferably concentrated sulfuric acid, chlorosulfonic acid, potassium 4-(1H-indol-3-yl)butanoate, 3-Indoleacetic acid, or Indole-3-butyric acid.

10. An ultrafiltration membrane manufactured according to the method of any one of the preceding claims, wherein the membrane comprises,

a dense top surface without observable pores,

a thin nanoporous active layer,

a macroporous supporting layer with asymmetrically porous channels within the cross section, and

a macroporous bottom surface.

11. A diffusion dialysis membrane manufactured according to the method of any one of any one of claims 1 to 10.

1/8

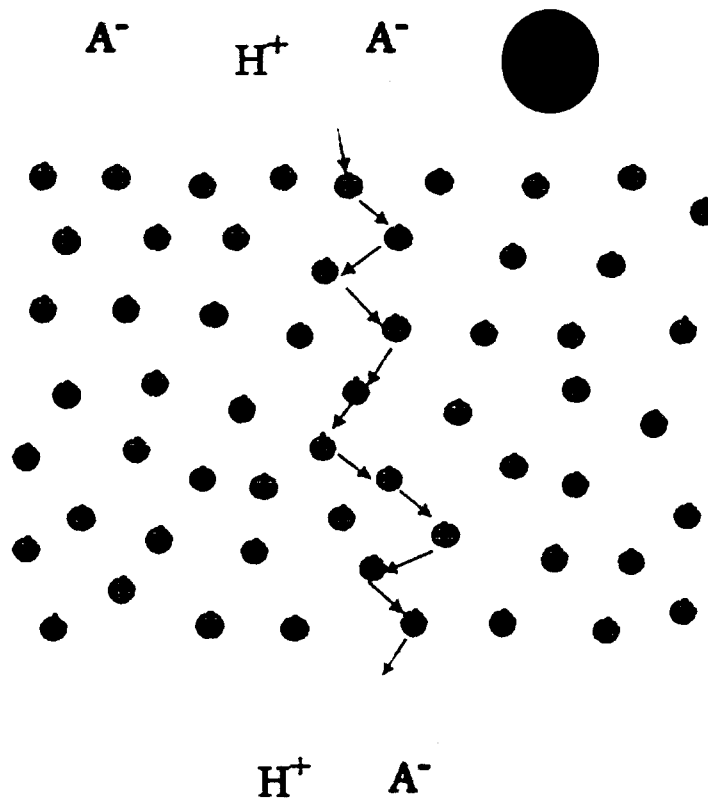


FIG. 1a

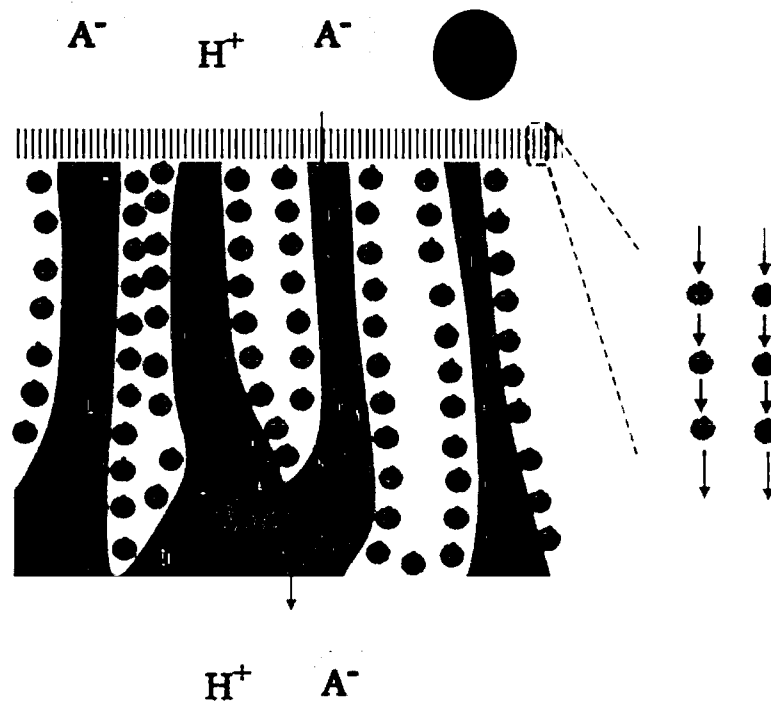


FIG. 1b

2/8

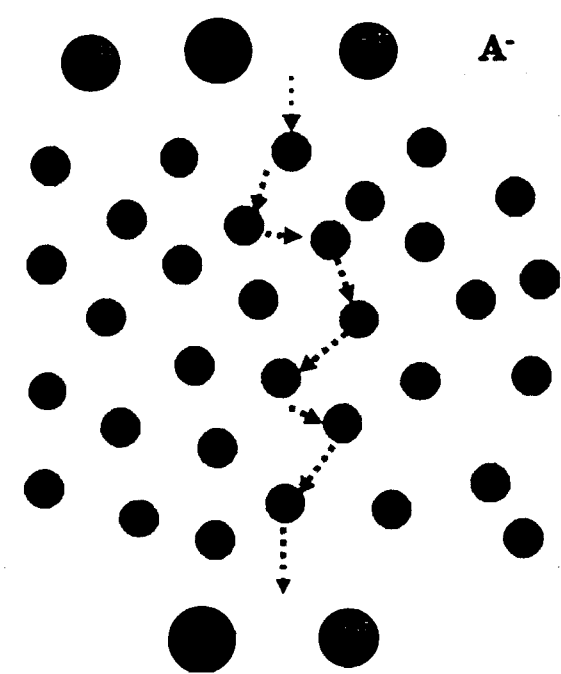


FIG. 2a

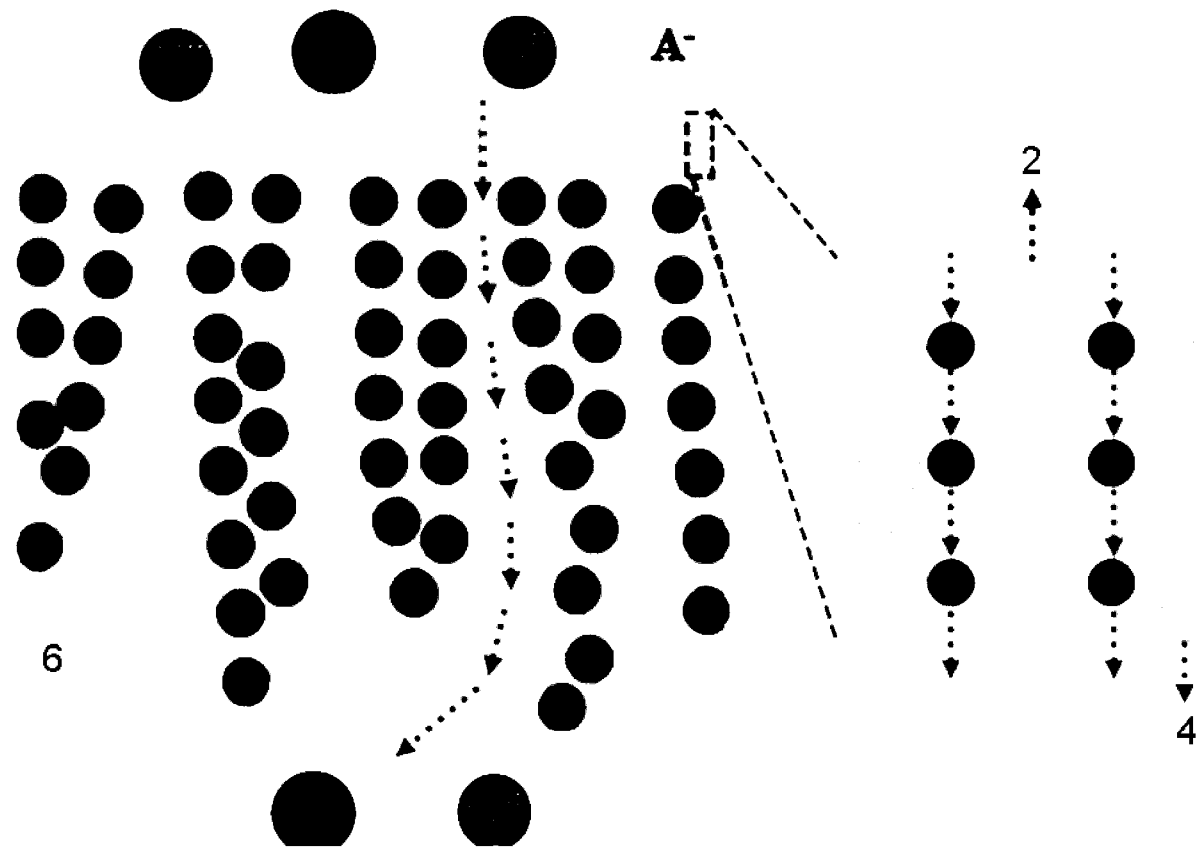


FIG. 2b

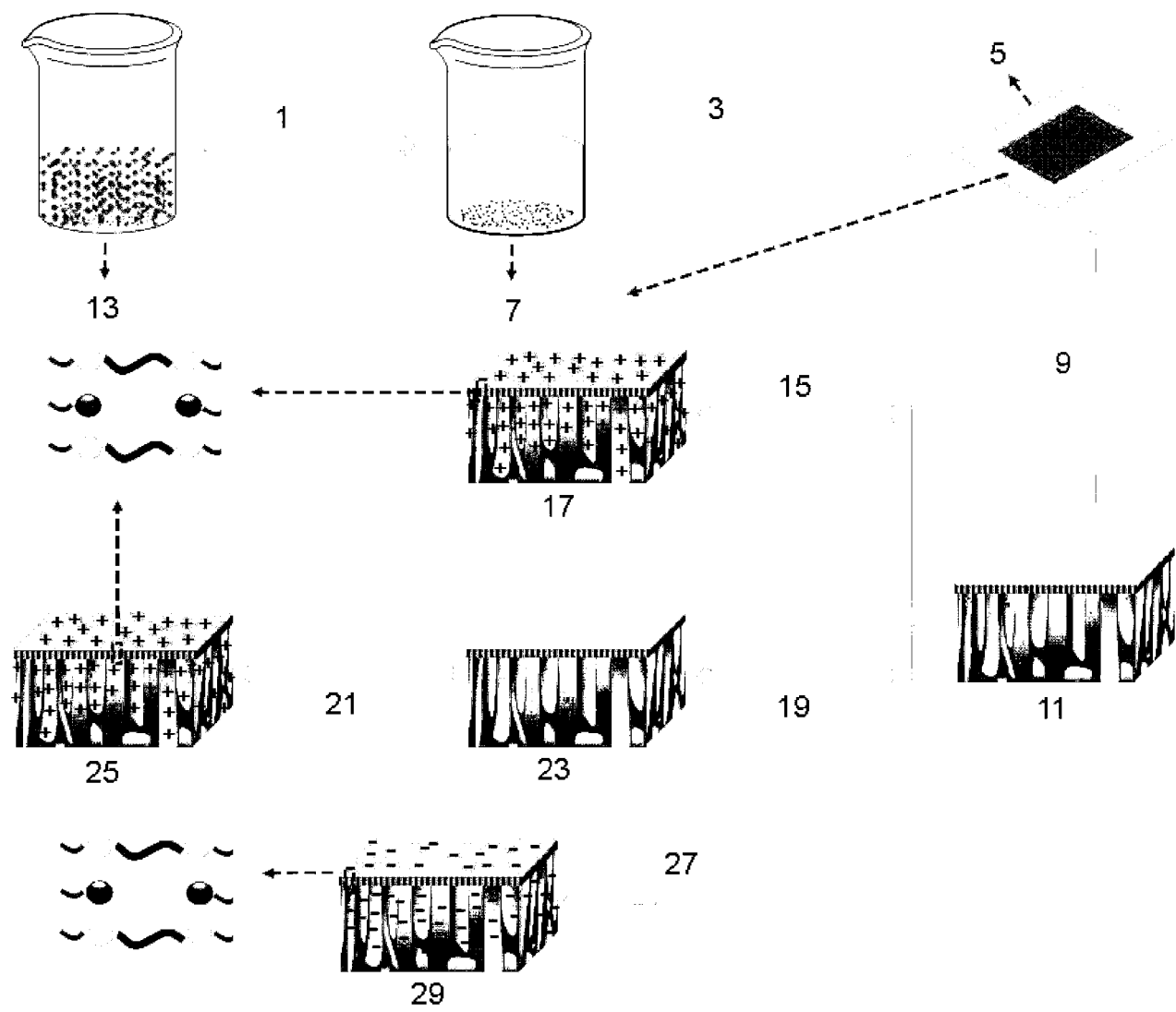
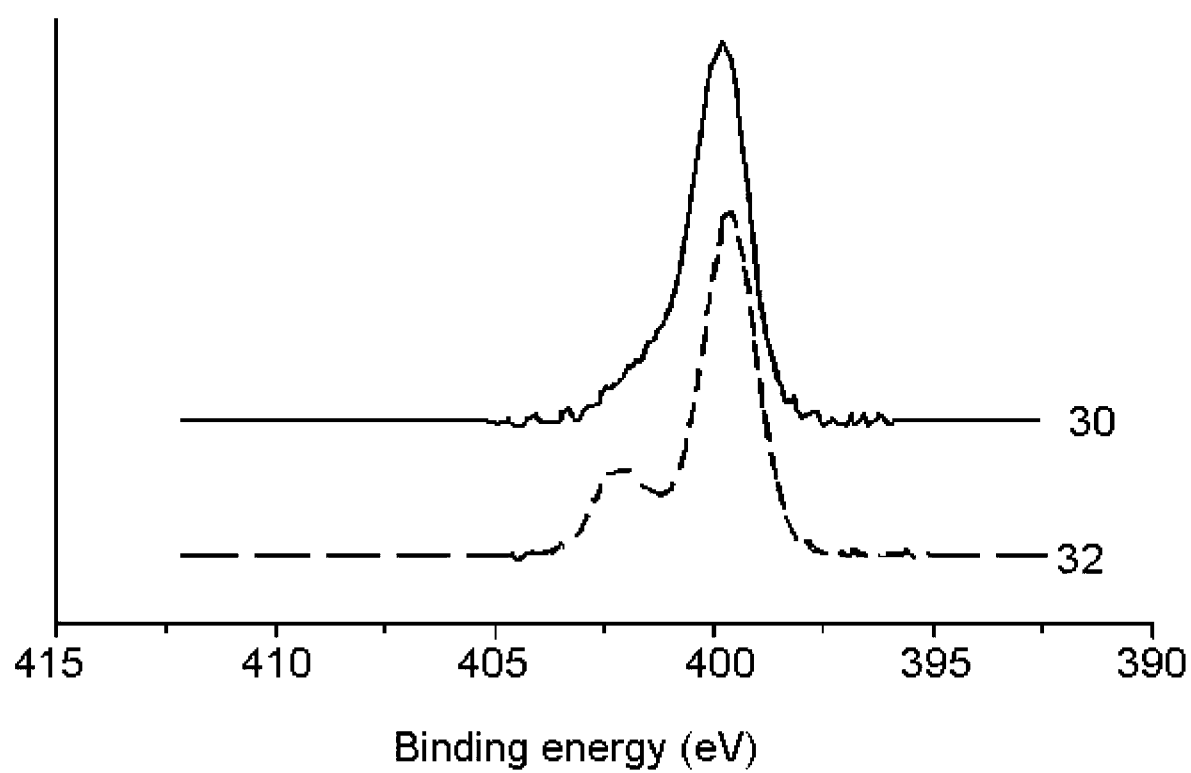


FIG. 3

**FIG. 4**

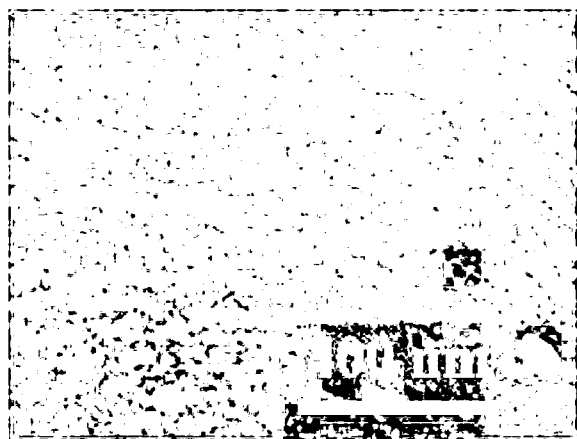


FIG. 5a



FIG. 5b

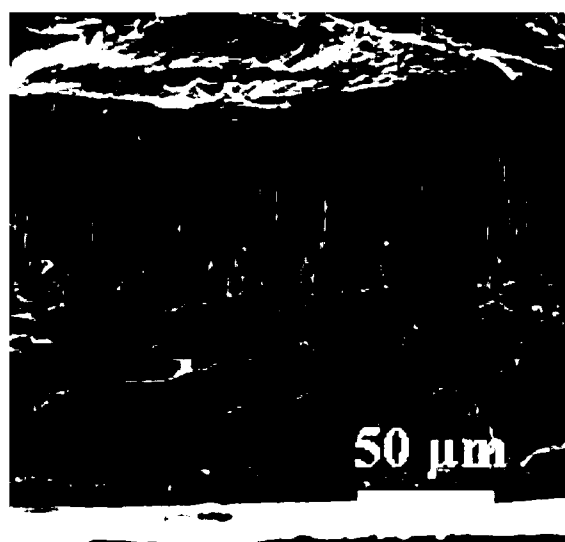


FIG. 5c

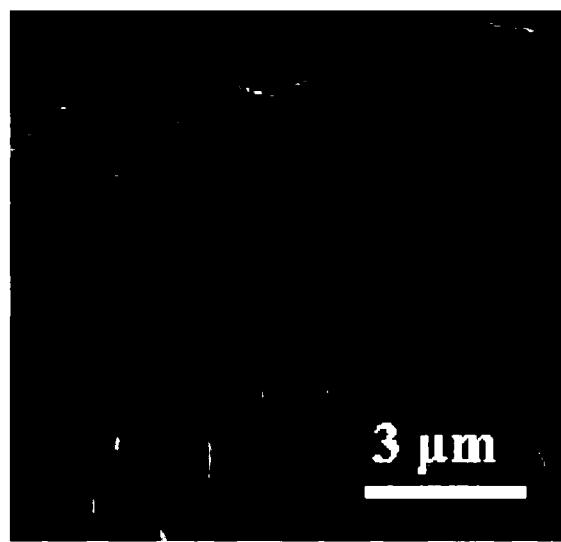
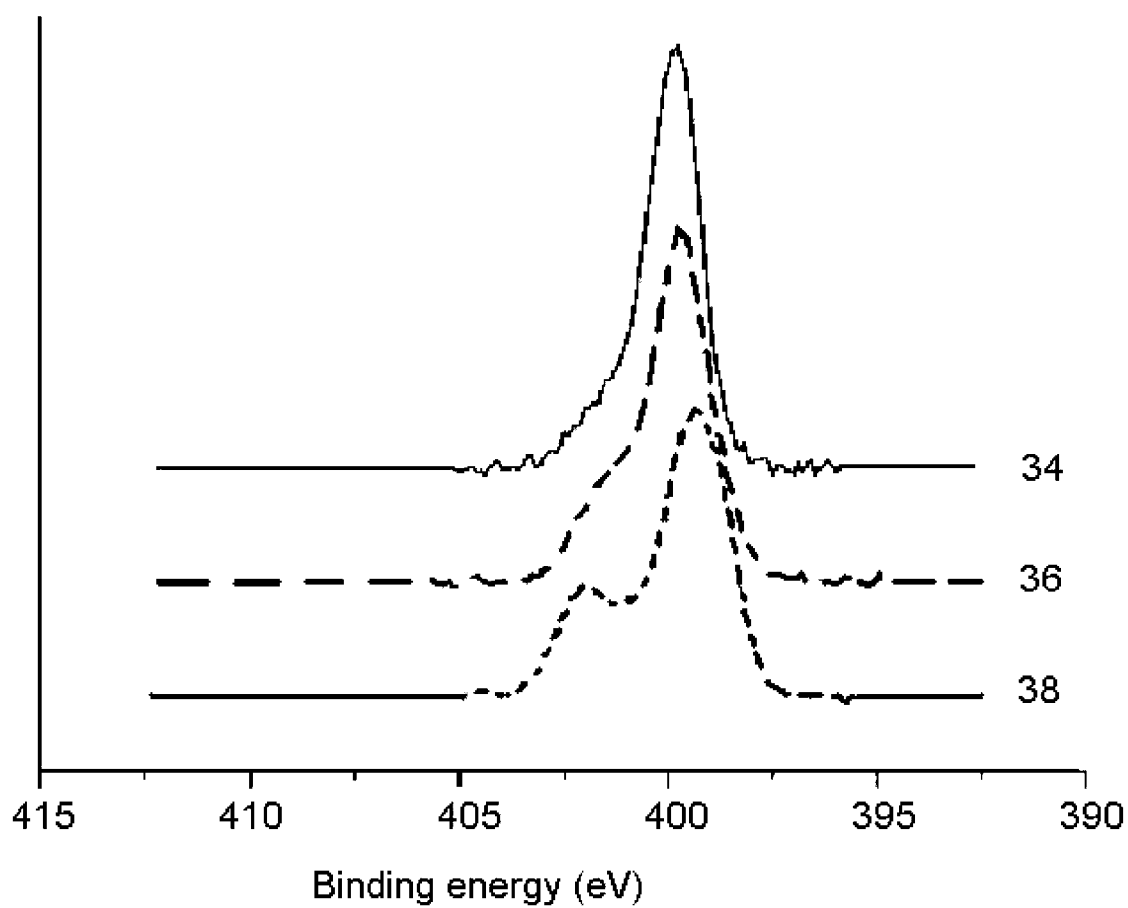


FIG. 5d

**FIG. 6**

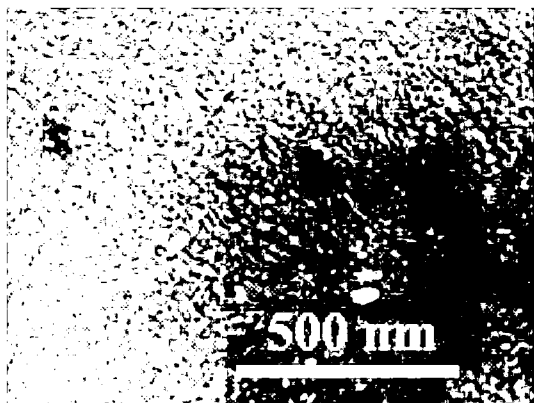


FIG. 7a

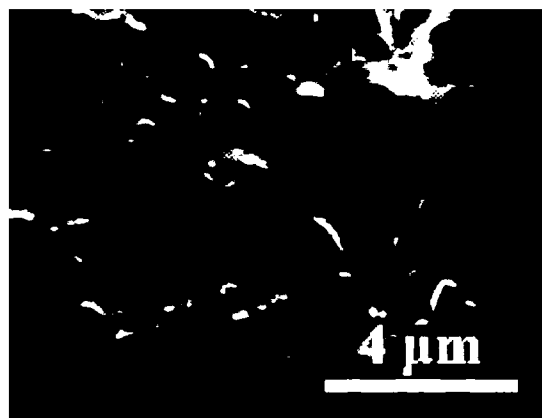


FIG. 7b

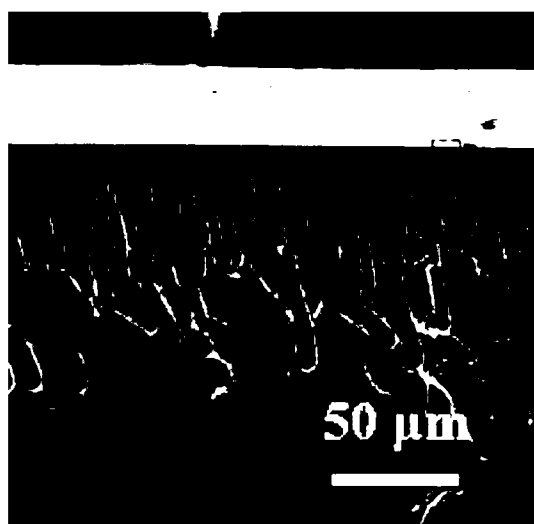


FIG. 7c

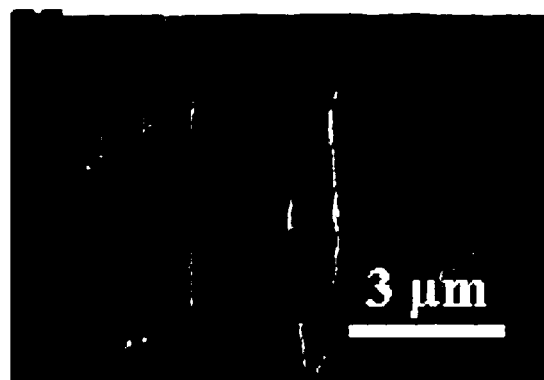


FIG. 7d

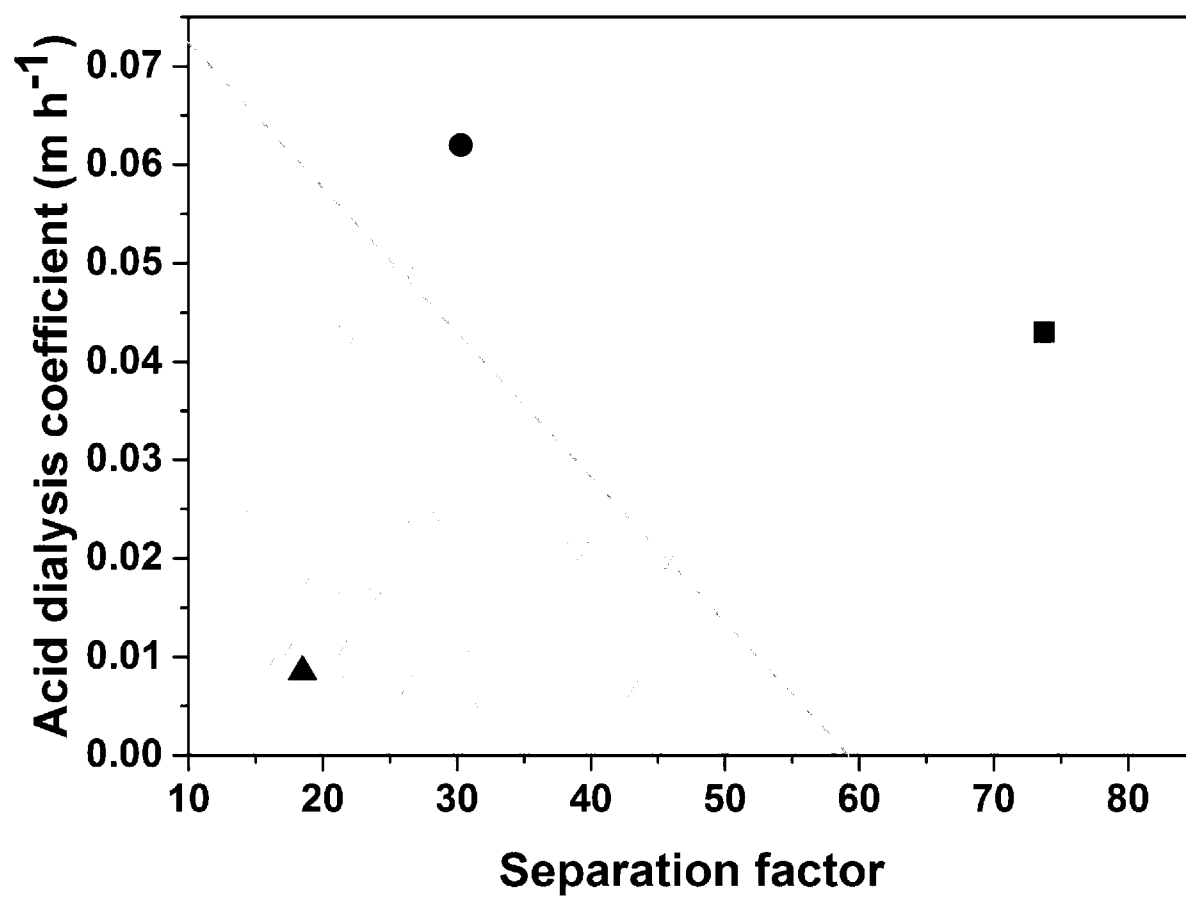


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2016/000370

A. CLASSIFICATION OF SUBJECT MATTER

B01D 69/00 (2006.01) B01D 71/00 (2006.01) B01D 67/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

B01DEPODOC & WPIAP: IPC and CPC marks: B01D61/low, B01D63/low, B01D65/low, B01D67/low, B01D69/low, B01D69/125/LOW, & B01D 71/00/low; Keywords: ultra-filtration, ion-exchange, Asymmetric, coagulate and similar terms

Applicant and Inventor names searched in ESPACENET, AusPat and Internal Databases provided by IP Australia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 23 December 2016		Date of mailing of the international search report 22 December 2016	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au		Authorised officer Santosh Gupta AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262837947	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2016/000370
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3855122 A (BOURGANEL) 17 December 1974 Abstract; col. 2, line 6; col. 2, line 5 - col. 3, line 42; col. 5, lines 48-69; col. 6, lines 21-66; claim 4; Tables 1-3	1-11
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Form PCT/ISA/210 (fifth sheet) (July 2009)

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2016/000370	
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End of Annex			
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INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2016/000370	
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Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
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