

A PREPARATION METHOD OF HOLLOW FIBER SEPARATION MEMBRANES WITH A DENSE-SELECTIVE LAYER

Technical Field

This invention relates to the technical field of membrane separation, in particular to a preparation method of hollow fiber separation membranes with a dense-selective layer.

Background

With rapid industrial development and expansion of population, problems including severe water environment pollution and fresh water resources shortage are brought at the same time of fast economic growth. Thus, seeking various methods to produce cleaned water becomes an urgent task, and traditional technology of water treatment (ion exchange, absorption, advanced oxidation, etc.) has problems of great energy consumption and complicated operation, easily leading to secondary water pollution. Compared with the prior art, the membrane separation method has advantages of high separation efficiency, low energy consumption, easy operation, and compact equipment, etc., and this technique has been widely applied in the following aspects: seawater desalination, wastewater treatment of chemical, food, medicine and electronic industry, municipal wastewater treatment, filtration of drinking water for home or commercial use.

At present, commercialized membrane products mainly are spiral-wound membranes and hollow fiber membranes, whereas manufacturing process of the spiral-wound membranes is rather complex and spiral wound membranes are confronted with difficulties including strict requirement on water quality, poor anti-fouling resistance, and incomplete contaminant removal during use. As a comparison, hollow fiber membranes have plenty of advantages, such as high packing density, compact component structure, small size and light weight, easy backwashing, and lower manufacturing cost, so the hollow fiber membranes attract more attention, and have more research value for practical applications.

Compared with hollow fiber membranes with rather big pore size, hollow fiber separation membranes with a dense-selective layer may be more widely applied in actual life, and existing hollow fiber separation membranes with a dense-selective layer are mainly produced through a composite method and a direct spinning method. The composite method refers to coating polymers on surface of ultrafiltration membranes and obtaining membranes with a dense-selective layer by crosslinking or interfacial polymerization. However, this manufacturing

technique of layer-by-layer coating and multistep interfacial polymerization has high investment cost, complex operation process and low production efficiency, and the produced membranes are unsuitable for backwashing because of low bonding strength between the coating and supporting layer. Moreover, in the composite method, direct coating process or interfacial polymerization cannot be conducted to obtain hollow fiber separation membranes with a dense-selective layer, and above operation may be conducted only if the ultrafiltration fiber membranes are dried with glycerin and then packed into the membrane module. By the direct spinning method, cellulose acetate, polyethyleneimine, polybenzimidazoles, polyvinylidene fluoride, and polyethersulfone, taken as polymeric membrane materials, are dissolved in the solvents with additives to get homogeneous spinning dope, and the hollow fiber membranes are obtained by phase inversion process. The advantages of this method are that continuous production may be achieved during the whole process and production efficiency is high. Defects of this method are as follows: with the limitation on the spinneret construction and the process design, pore size distribution of produced membrane products is uneven, and the thickness of selective layer with this method is far more than the thickness of selective layer with the composite method, therefore, the pore size of membrane is rather big and membrane flux is rather low.

Therefore, it is necessary to provide an advanced method to overcome the defects in the prior art.

Summary of the Invention

(I) Technical problems solved

With regard to the defects existing in the prior art, this invention provides a preparation method of hollow fiber separation membranes with a dense-selective layer. By one-step spinning method, the following problems, including high investment cost on the manufacturing technique, complex operation process, low production efficiency, the produced membrane unsuitable for backwashing, uneven distribution of pore size, and low yield rate, that exists in the composite method can be solved.

(II) Technical scheme

In order to realize the above stated objectives, this invention discloses the following technical scheme: a preparation method of hollow fiber separation membranes with a dense-selective layer, including the following steps:

S1. Preparing spinning dope: put membrane materials, additives and organic solvents into a dissolving tank and mix them for a time t under a temperature T and a rotate speed r to obtain polymer solution. Put above polymer solution into a degassing tank, and let it stand for a period of time to degas under a vacuum or pressurized nitrogen condition, until membrane materials are completely dissolved and there is no bubble; repeat the above operations to obtain multiple types of spinning dopes;

S2. Spinning hollow fiber membranes: utilize a multi-channel spinneret, including a bore fluid channel, spinning dope channels of supporting layers, and spinning dope channels of separation layers, wherein, both the spinning dope channels of supporting layers and separation layers have one or more; the end of bore fluid channel is located in a central zone, and the spinning dope channels of supporting layers and separation layers form an exchange zone with bore fluid channels at the end of bore fluid channels; after the spinning dopes of supporting layers and/or separation layers experience sufficient chemical crosslinking in the exchange zone, nascent membrane extruded from the spinneret enters the external coagulating bath; multiple types of spinning dopes without impurity and bubbles, which are obtained by pretreatment in step S1, are extruded simultaneously from the multi-channel spinneret in a certain proportion, then enter a coagulating bath for phase inversion process under certain conditions of a bore fluid flow rate and an air-gap distance, to be solidified into membranes. After that, a further solvent exchange is performed in the next coagulating bath, followed by a washing to obtain the hollow fiber membrane intermediates. Finally, membrane intermediates are wound on a fiber-collecting roller;

S3. Post-treatment: put the membrane intermediates from S2 in a post-treatment tank for heat setting, after that a pore-protecting agent is used to replace the water in the membrane to prevent membrane pores collapsing, therefore wet membranes are produced. Hollow fiber separation membranes with a dense-selective layer may be obtained after the process of drying the wet membranes.

As a preferred technical scheme, “put membrane materials, additives and organic solvents into a dissolving tank” stated in step S1 is detailed as follows: taking 10-35phr membrane materials, 10-50phr additives, 30-80phr organic solvents and putting them into the dissolving tank.

As a preferred technical scheme, the membrane materials stated in step S1 are polymer

materials, and the membrane materials are at least one of the following materials: polyvinylidene fluoride, polyethersulfone, polysulfone, polyacrylonitrile, polydimethylsiloxane, polybenzimidazoles, polyamide, polyimide, polyethyleneimine, and cellulose acetate.

As a preferred technical scheme, the additives stated in step S1 are pore-forming agents or thickeners, and the additives are at least one of the following materials: polyethylene glycol (PEG), diethylene glycol (DEG), ethylene glycol (EG), polyvinyl pyrrolidone (PVP), lithium chloride (LiCl), and lithium bromide (LiBr).

As a preferred technical scheme, the organic solvents stated in step S1 are one of the following organic solvents: n-methylpyrrolidone (NMP), n,n-dimethylacetamide (DMAC), n,n-dimethylformamide (DMF), tetrahydrofuran (THF).

As a preferred technical scheme, in the stated step S1, the temperature T is in the range of room temperature to 80 °C; the rotate speed is 20-300 r/min; the time t is 12-48 hours.

As a preferred technical scheme, the coagulating baths stated in step S2 include No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath, which are interconnected, wherein, there is running water in the No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath. The water starts from the No.1 coagulating bath, flows through the No.2 coagulating bath, enters the No.3 coagulating bath, and flows out of the No.3 coagulating bath; a heating device and a uniform distributing baffle with continuous flow are provided in the No.1 coagulating bath; heating devices are also provided in both the No.2 and No.3 coagulating baths; phase inversion process is proceeded in the No.1 coagulating bath, which enables solidification of nascent membranes, and solvent exchange is conducted in the No.2 coagulating bath, followed by a washing in the No.3 coagulating bath to obtain the hollow fiber membrane intermediates. Finally, membrane intermediates are winded on a fiber-collecting roller.

As a preferred technical scheme, the multiple spinning dopes without impurity and bubbles, stated in step S2, include spinning dopes of supporting layers and separation layers, wherein, proportion of the spinning dopes for supporting layers is 80-100, and proportion of the spinning dopes for separation layers is 0-20; the spinning dopes of the supporting layers include one or multitype, and the spinning dopes of the separation layers include one or multitype; the bore fluid flow rate is 1-30 ml/min, and the air-gap distance is 0-40 cm.

As a preferred technical scheme, in the stated step S2, water temperature of the coagulating baths is in the range of room temperature to 80 °C.

As a preferred technical scheme, heat-setting temperature stated in step S3 is in the range of room temperature to 120 °C, and duration lasts 0-18 hours.

(III) Beneficial effects

This invention provides a preparation method of hollow fiber separation membranes with a dense-selective layer. The method has the following beneficial effects:

1. A preparation method of hollow fiber separation membranes with a dense-selective layer in this invention, by which hollow fiber separation membranes with a dense-selective layer are obtained through one-step phase inversion process on a dry-wet spinning production line, shortens technological process, meanwhile reduces investments in process equipment as well as chemicals consumption costs, and is easy for industrial production.

2. A preparation method of hollow fiber separation membranes with a dense-selective layer in this invention, by which prepared spinning dopes are extruded from a multi-channel spinneret in a specific proportion, and phase inversion and interfacial crosslinking are achieved at the same time of spinning, not only allows the spinning dope of separation layer before the phase inversion to conduct on-line chemical crosslinking on interface of a supporting layer under liquid state for the formation of dense-selective layer, but also makes the crosslinking occur more easily and more sufficiently to ensure no delamination between the supporting layer and separation layer, for the reason that materials before the phase inversion are still in liquid phase. Through the method in this invention, the preparation of hollow fiber separation membranes with a dense-selective layer may be achieved by one step, compactness of produced hollow fiber membranes may be adjusted, and no membrane delamination will occur. Yield rate of membrane products through the preparation method stated in this invention may achieve more than 99%.

3. A preparation method of hollow fiber separation membranes with a dense-selective layer in this invention enables a wide variety of application for its resulted membrane products and has no special requirements and limitation on membrane materials; according to the actual demand of membrane products, hollow fiber membrane with a dense-selective layer and evenly distributed pores may be obtained through the selection of proper types and concentrations of polymer membrane materials, organic solvents and additives, as well as the adjustment of

spinning process parameters. Moreover, flux and molecular weight cutoff (MWCO) of the hollow fiber membranes may be adjusted by optimizing formation of spinning dopes and spinning process parameters to produce hollow fiber separation membranes with a dense-selective layer, which are suitable for various application fields (pervaporation, gas separation, ultrafiltration, nanofiltration, reverse osmosis, membrane distillation, forward osmosis). Accordingly, the hollow fiber membranes produced through the method in this invention have various types and may be widely used.

4. As a preferred technical scheme, a preparation method of hollow fiber separation membranes with a dense-selective layer in this invention, may still provide No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath, through special design of coagulating baths, wherein, fresh water moves up from the bottom of No.1 coagulating bath and overflows into the No.2 coagulating bath, then enters the No.3 coagulating bath from the bottom of No.2 coagulating bath, and finally flows out of the No.3 coagulating bath; It avoids the situation in which the concentration of the static water in the coagulating baths rises up caused by solvent exchange as time goes by and thus the membrane products performance may be impacted in the prior arts; this method ensures stability of the solution concentration during the solvent exchange, for which performance of the produced membrane products may be more stable.

Description of the Drawings

Fig.1 is a manufacturing flow chart showing detailed embodiments for a preparation method of hollow fiber separation membrane with a dense selective layer stated in this invention.

Fig.2 is a schematic diagram showing the structure of the multi-channel spinneret in the embodiments for a preparation method of hollow fiber separation membrane with a dense selective layer stated in this invention.

Detailed Description of the Preferred Embodiments

The technical scheme of the embodiments in this invention will be described clearly and completely as follows by combining the drawings of the embodiments, but obviously, the described embodiments are only a part of the embodiments in this invention, rather than total embodiments. Based on the embodiments in this invention, all of other embodiments that one skilled in the art obtains without spending any creative effort belong to the protection scope of

this invention.

As shown in Fig. 1, a preparation method of hollow fiber separation membrane with a dense selective layer stated in this invention includes the following steps:

S1. Preparing spinning dope: put membrane materials, additives and organic solvents into a dissolving tank and mix them for a time t under a temperature T and a rotate speed r to obtain polymer solution. Put above polymer solution into a degassing tank, and let it stand for a period of time to degas under a vacuum or pressurized nitrogen condition, until membrane materials are completely dissolved and there is no bubble; repeat the above operations to obtain multiple types of spinning dopes; In order to ensure that the membrane materials are completely dissolved and there is no bubble, during the manufacturing process, the time of degassing under a vacuum or pressurized nitrogen condition is normally 12-24 hours.

S2. Spinning hollow fiber membranes: as shown in Fig. 2, utilize a multi-channel spinneret, including a bore fluid channel, spinning dope channels of supporting layers, and spinning dope channels of separation layers, wherein, both the spinning dope channels of supporting layers and separation layers have one or more; the end of bore fluid channel is located in a central zone, and the spinning dope channels of supporting layers and separation layers form an exchange zone with bore fluid channels at the end of bore fluid channels; after the spinning dopes of supporting layers and/or separation layers experience sufficient chemical crosslinking in the exchange zone, nascent membrane extruded from the spinneret enters the external coagulating bath; multiple types of spinning dopes without impurity and bubbles, which are obtained by pretreatment in step S1, are extruded simultaneously from the multi-channel spinneret in a certain proportion, then enter a coagulating bath for phase inversion process under certain conditions of a bore fluid flow rate and an air-gap distance, to be solidified into membranes. After that, a further solvent exchange is performed in the next coagulating bath, followed by a washing to obtain the hollow fiber membrane intermediates. Finally, membrane intermediates are winded on a fiber-collecting roller. The bore fluid may be obtained by mixing organic solvents and water in proportion. During the manufacture, the spinning dopes and the bore fluid are extruded from the multi-channel spinneret, and it is necessary to provide a certain driven pressure for the spinning dope by using one of a precision gear pump, a plunger pump, and a diaphragm pump, so as to ensure that the spinning dopes in the material tank enters the spinneret under the driven pressure; because the flow rate of bore

fluid determines the molding of hollow fiber separation membranes with a dense-selective layer in this invention, it is unnecessary to provide great extruding pressure, but to control the flow rate of bore fluid precisely. In this case, a precision metering pump is used to achieve above requirements. Normally, for a utilized multi-channel spinneret, the bore fluid channel is in the innermost layer, the spinning dope channel of supporting layer is provided in the intermediate layer, and the spinning dope channel of separation layer is provided in the outermost layer; the design of multi-channel spinneret for a preparation method in this invention may ensure that the spinning dope of supporting layers used to produce the supporting layers and the spinning dope of separation layers used to produce the separation layers are injected through different channels respectively; the spinning dope starts to proceed the solvent exchange with the bore fluid at the spinneret nozzle and the formation of hollow fiber membrane can be achieved by one step; the crosslinking occurs more easily and more sufficiently to ensure no delamination between the supporting layer and separation layer, for the reason that materials before the phase inversion are still in liquid phase. As for the structure of multi-channel spinneret shown in Fig. 2, the spinning dope channels of the separation layers include two channels, namely, the spinning dope channel 3 of the separation layers and the secondary spinning dope channel 4 of the separation layers. What should be noticed is that Fig. 2 only aims to show the structure of multi-channel spinneret, wherein, the amount of the spinning dope channel 2 of the supporting layer and the spinning dope channel 3 of the separation layer are not used to define the specific amount of the spinning dope channels of the supporting layers and the spinning dope channels of the separation layers in the multi-channel spinneret for a preparation method of hollow fiber separation membrane with a dense selective layer in this invention.

S3. Post-treatment: put the membrane intermediates from S2 in a post-treatment tank for heat setting, after that a pore-protecting agent is used to replace the water in the membrane to prevent membrane pores collapsing, therefore wet membranes are produced. Hollow fiber separation membranes with a dense-selective layer may be obtained after the process of drying the wet membranes. During the actual manufacture, a step of hydrophilization treatment may be performed after heat setting, based on whether hollow fiber separation membranes with a dense-selective layer in this invention have requirements on hydrophilicity or not, and if hydrophilicity is required, the hydrophilization treatment may be conducted after heat setting,

so as to improve anti-fouling performance of the membrane products.

With the preparation method in this invention, prepared spinning dopes are extruded from a multi-channel spinneret with 3-5 channels or even more, and that spinneret provides a bore fluid channel, one or more spinning dope channels of supporting layers, and one or more spinning dope channels of separation layers based on needs. Meanwhile, multiple spinning dopes in multiple spinning dope channels of the supporting layers may perform chemical crosslinking, and multiple spinning dopes in multiple spinning dope channels of the separation layer may also perform chemical crosslinking. The spinning dope channels of supporting layers and separation layers form an exchange zone with the bore fluid channel finally, and dopes in the channels, after performing on-line chemical crosslinking, are extruded and enter the coagulating baths. Finally, hollow fiber membrane intermediates are produced by solvent exchange. By adopting this integrated design, it may be ensured that spinning dope used to produce the supporting layers and spinning dope used to produce the separation layers are injected through different channels respectively, and the spinning dope starts to proceed the solvent exchange with the bore fluid at the spinneret nozzle to make the formation of hollow fiber membrane achieved by one step; for the reason that materials before the phase inversion are still in liquid phase, the crosslinking occur more easily and more sufficiently to ensure a strong bonding between the supporting layer and separation layer, and thus the delamination for the produced membrane products can be avoided. In the embodiment, the coagulating baths include No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath, which are interconnected, wherein, there is running water in the No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath. The fresh water starts from the No.1 coagulating bath, flows through the No.2 coagulating bath, enters the No.3 coagulating bath, and flows out of the No.3 coagulating bath. Phase inversion process is proceeded in the No.1 coagulating bath, which enables solidification of nascent membranes, and solvent exchange is proceeded in the No.2 coagulating bath, followed by a washing in the No.3 coagulating bath to obtain the hollow fiber membrane intermediates. Finally, membrane intermediates are winded on a fiber-collecting roller. During actual manufacturing process, nascent membranes may perform solvent exchange in the No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath, so the functions description of No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath in this application only aims to define the main functions of each coagulating

bath, and has no limitation on other reactions occurring in each coagulating bath. A preparation method of hollow fiber separation membranes with a dense-selective layer in this invention, provides No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath, wherein, water moves up from the bottom of No.1 coagulating bath and overflows into the No.2 coagulating bath, then enters the No.3 coagulating bath from the bottom of No.2 coagulating bath, and finally flows out of the No.3 coagulating bath. This ensures a stable solution concentration during the solvent exchange, and flowing water in the coagulating baths avoids the situation in which the solution concentration of the coagulating bath rises up caused by solvent exchange as time goes by, accordingly impairing the performance of membrane products in the prior arts. Comparatively, the performance of membrane products produced with the preparation method in this invention may be more stable. In practical application, the coagulating baths of a preparation method of hollow fiber separation membrane with a dense selective layer in this invention may also include one or more, in which flowing water is provided, and flows in from the bottom and out of the top. This may also achieve the technical effect of this invention, without affecting presentation of the advantages in this invention.

In actual manufacturing process, membrane materials, additives, and organic solvents are common materials in the membrane manufacturing field, and materials, as well as proportion, may be added based on actual needs of the membrane products. The proportions of membrane materials, additives, and organic solvents are as follows: membrane materials 10-35phr, additives 10-50phr, organic solvents 30-80phr. Membrane materials, additives, and organic solvents may be chosen based on actual needs. For example, the membrane materials are at least one of the following polymer materials: polyvinylidene fluoride, polyethersulfone, polysulfone, polyacrylonitrile, polydimethylsiloxane, polybenzimidazoles, polyamide, polyimide, polyethyleneimine, and cellulose acetate; the additives are at least one of the following pore-forming agents or thickeners: polyethylene glycol (PEG), diethylene glycol (DEG), ethylene glycol (EG), polyvinyl pyrrolidone (PVP), lithium chloride (LiCl), and lithium bromide (LiBr); the organic solvents are one of the following organic solvents: n-methylpyrrolidone (NMP)、n,n-dimethylacetamide (DMAC)、n,n-dimethylformamide (DMF)、tetrahydrofuran (THF). It should be noted that, the above materials are only examples, and other membrane materials, additives and organic solvents may also be chosen based on actual manufacturing needs, which has no effect on presentation of the advantages in this

invention, and belongs to the protection scope disclosed in Claim 1. During the manufacturing process, preparation parameters of the spinning dope may be adjusted based on actual needs. For example, in the stated step S1, the temperature T is in the range of room temperature to 80 °C; the rotate speed is set to 20-300 r/min; the time t is set to 12-48 hours.

In order to further optimize coagulating bath design, in the embodiments stated in this invention, depth of the No. 1 coagulating bath is identical with depth of the No. 2 and No. 3 coagulating baths; meanwhile, heating devices are provided in the No.1, No. 2, and No. 3 coagulating baths, so as to maintain temperature of the three coagulating baths in the range of room temperature to 80 °C, which may maximize efficiency during the solvent exchange, and enhance effect of the solvent exchange. A uniform distributing baffle with continuous flow is provided in the No.1 coagulating bath to further optimize liquidity of solution and prevent fluctuation caused by rapid flow from affecting phase-inversion process. Corresponding settings of three coagulating baths in the embodiments may further improve stability of the solution concentration, and make sure little concentration fluctuation in these three coagulating baths, which ensures stability and effect of the phase inversion and solvent exchange during the membrane manufacturing process.

During the membrane manufacturing process, the flux and molecular weight cutoff (MWCO) of hollow fiber membranes can be adjusted according to membrane product needs and application field by optimizing formation of the spinning dopes and spinning process parameters to produce hollow fiber separation membranes with a dense-selective layer, which are suitable for various application fields (pervaporation, gas separation, ultrafiltration, nanofiltration, reverse osmosis, membrane distillation, forward osmosis). For instance, the spinning dopes include spinning dopes of supporting layers and separation layers, wherein, proportion of the spinning dopes for supporting layers may be 80-100, and proportion of the spinning dopes for separation layers may be 0-20. The spinneret in the embodiment includes 3-5 channels and even more, and that spinneret provides a bore fluid channel, one or more spinning dope channels of supporting layers, and one or more spinning dope channels of separation layers, which accounts for that both the spinning dopes of supporting layers and separation layers may include one or more types. As shown in Fig. 1, in the embodiments, the spinning dopes of supporting layers include spinning dope A and spinning dope B, and the spinning dopes of separation layers include spinning dope C and spinning dope D. For practical

application, channels number of the spinneret, the types and amount of the spinning dopes for the supporting layers and the separation layers may be adjusted specifically according to actual needs. In step S2, the flow rate of bore fluid is 1-30 ml/min, and the air-gap distance between the spinneret and the No. 1 coagulating bath is 0-40 cm. In step S3, heat-setting temperature is in the range of room temperature to 120 °C, and duration lasts 0-18 hours.

Embodiment 1:

In step S1, the membrane materials are polyvinylidene fluoride and polyimide; the additive is polyethylene glycol (PEG); the organic solvent is n-methylpyrrolidone (NMP); the proportions are as follows: 20phr membrane materials, 14phr additives, and 66phr organic solvents. Temperature T is 65 °C, rotate speed is 60 r/min, and time t is 24 hours.

In step S2, spinning dopes without impurity and bubbles include polyvinylidene fluoride spinning dope and polyimide spinning dope, and proportion of each spinning dope is 5:1; the flow rate of mixed spinning dopes is 15 ml/min, the flow rate of bore fluid is 7.5 ml/min, and the air-gap distance is 5 cm. The temperature of solution in the No. 1 coagulating bath is 35 °C.

In step S3, heat-setting temperature is 80°C, and duration lasts 8 hours.

Through steps S1, S2, S3, hollow fiber separation membranes with a dense-selective layer are produced.

Embodiment 2:

In step S1, the membrane materials are polyethersulfone, polyacrylonitrile, and polybenzimidazoles; the additive is polyvinyl pyrrolidone (PVP); the organic solvent is n,n-dimethylacetamide (DMAC); the proportions are as follows: 25phr membrane materials, 30phr additives, and 45phr organic solvents. Temperature T is 50 °C, rotate speed is 240 r/min, and time t is 12 hours.

In step S2, spinning dopes without impurity and bubbles include polyethersulfone spinning dope, polyacrylonitrile spinning dope, and polybenzimidazoles spinning dope, and proportion of each spinning dope is 4:3:1; the flow rate of mixed spinning dopes is 12 ml/min, the flow rate of bore fluid is 5 ml/min, and the air-gap distance is 10 cm. The temperature of solution in the No. 1 coagulating bath is 40 °C.

In step S3, heat-setting temperature is 120 °C, and duration lasts 12 hours.

Through steps S1, S2, S3, hollow fiber separation membranes with a dense-selective layer are produced.

Embodiment 3:

In step S1, the membrane materials are polyacrylonitrile, cellulose acetate, polydimethylsiloxane, and polyethyleneimine; the additive is lithium chloride (LiCl); the organic solvent is n,n-dimethylformamide (DMF); the proportions are as follows: 18phr membrane materials, 30phr additives, and 52phr organic solvents. Temperature T is 80 °C, rotate speed is 150 r/min, and time t is 48 hours.

In step S2, spinning dopes without impurity and bubbles include polyacrylonitrile spinning dope, cellulose acetate spinning dope, polydimethylsiloxane spinning dope, and polyethyleneimine spinning dope, and proportion of each spinning dope is 5:3:1:1; the flow rate of mixed spinning dopes is 20 ml/min, the flow rate of bore fluid is 10 ml/min, and the air-gap distance is 15 cm. The temperature of solution in the No. 1 coagulating bath is 50 °C.

In step S3, heat-setting temperature is 50 °C, and duration lasts 18 hours.

Through steps S1, S2, S3, hollow fiber separation membranes with a dense-selective layer are produced.

The following table is a statistical table of the hollow fiber separation membranes with a dense-selective layer produced according to Embodiment 1, 2, 3:

	Membrane materials	Types of membranes	Yield rate of membrane products
Embodiment 1	polyvinylidene fluoride and polyimide	nanofiltration membrane	99.5%
Embodiment 2	polyethersulfone, polyacrylonitrile, and polybenzimidazoles	forward osmosis membrane	99.3%
Embodiment 3	polyacrylonitrile, cellulose acetate, polydimethylsiloxane, and polyethyleneimine	reverse osmosis membrane	99.2%

As shown in the above table, a preparation method of hollow fiber separation membranes with a dense-selective layer in this invention, which produces hollow fiber separation membranes with a dense-selective layer through one-step phase inversion process on a dry-wet spinning production line, shortens technological process; meanwhile, it enables a wide variety of application for its resulted membrane products; membrane materials, additives, organic solvents and preparation parameters may be adjusted according to actual manufacturing needs; moreover, by optimizing formation of spinning dopes and spinning process parameters, flux and molecular weight cutoff (MWCO) of the hollow fiber membranes may be adjusted to

produce hollow fiber separation membranes with a dense-selective layer, which are suitable for various application fields (pervaporation, gas separation, ultrafiltration, nanofiltration, reverse osmosis, membrane distillation, forward osmosis); besides, the yield rate of the membrane products is higher than 99%. A preparation method of hollow fiber separation membranes with a dense-selective layer in this invention has advantages such as low production costs, high production efficiency, wide application, and high yield rate.

Although embodiments of this invention have been shown and described, for one skilled in the art, it should be understood that these embodiments may be changed, amended, replaced and transformed without violating the principles and spirits of this invention, and the protection scope of this invention is determined by the claims and its equivalents.

Claims

1. A preparation method of hollow fiber separation membranes with a dense-selective layer, is disclosed, which is characterized in including the following specific steps:

S1. Preparing spinning dope: put membrane materials, additives and organic solvents into a dissolving tank and mix them for a time t under a temperature T and a rotate speed r to obtain polymer solution. Put above polymer solution into a degassing tank, and let it stand for a period of time to degas under a vacuum or pressurized nitrogen condition, until membrane materials are completely dissolved and there is no bubble; repeat the above operations to obtain multiple types of spinning dopes;

S2. Spinning hollow fiber membranes: utilize a multi-channel spinneret, including a bore fluid channel, spinning dope channels of supporting layers, and spinning dope channels of separation layers, wherein, both the spinning dope channels of supporting layers and separation layers have one or more; the end of bore fluid channel is located in a central zone, and the spinning dope channels of supporting layers and separation layers form an exchange zone with bore fluid channels at the end of bore fluid channels; after the spinning dopes of supporting layers and/or separation layers experience sufficient chemical crosslinking in the exchange zone, nascent membrane extruded from the spinneret enters the external coagulating bath; multiple types of spinning dopes without impurity and bubbles, which are obtained by pretreatment in step S1, are extruded simultaneously from the multi-channel spinneret in a certain proportion, then enter a coagulating bath for phase inversion process under certain conditions of a bore fluid flow rate and an air-gap distance, to be solidified into membranes. After that, a further solvent exchange is performed in the next coagulating bath, followed by a washing to obtain the hollow fiber membrane intermediates. Finally, membrane intermediates are winded on a fiber-collecting roller;

S3. Post-treatment: put the membrane intermediates from S2 in a post-treatment tank for heat setting, after that a pore-protecting agent is used to replace the water in the membrane to prevent membrane pores collapsing, therefore wet membranes are produced. Hollow fiber separation membranes with a dense-selective layer may be obtained after the process of drying the wet membranes.

2. According to the preparation method of hollow fiber separation membranes

with a dense-selective layer stated in Claim 1, its characteristics are that: “put membrane materials, additives and organic solvents into a dissolving tank” stated in step S1 is detailed as follows: taking 10-35phr membrane materials, 10-50phr additives, 30-80phr organic solvents and putting them into the dissolving tank.

3. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: the membrane materials stated in step S1 are polymer materials, and the membrane materials are at least one of the following materials: polyvinylidene fluoride, polyethersulfone, polysulfone, polyacrylonitrile, polydimethylsiloxane, polybenzimidazoles, polyamide, polyimide, polyethyleneimine, and cellulose acetate.

4. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: the additives stated in step S1 are pore-forming agents or thickeners, and the additives are at least one of the following materials: polyethylene glycol (PEG), diethylene glycol (DEG), ethylene glycol (EG), polyvinyl pyrrolidone (PVP), lithium chloride (LiCl), and lithium bromide (LiBr).

5. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: the organic solvents stated in step S1 are one of the following organic solvents: n-methylpyrrolidone (NMP), n,n-dimethylacetamide (DMAC), n,n-dimethylformamide (DMF), tetrahydrofuran (THF).

6. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: in the stated step S1, the temperature T is in the range of room temperature to 80 °C; the rotate speed is 20-300 r/min; the time t is 12-48 hours.

7. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: the coagulating baths stated in step S2 include No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath, which are interconnected, wherein, there is running water in the No.1 coagulating bath, No.2 coagulating bath, and No.3 coagulating bath. The water starts from the No.1 coagulating bath, flows through the No.2 coagulating bath, enters the No.3 coagulating bath, and flows out of the No.3 coagulating bath; a heating device and a

uniform distributing baffle with continuous flow are provided in the No.1 coagulating bath; heating devices are also provided in both the No.2 and No.3 coagulating baths; phase inversion process is proceeded in the No.1 coagulating bath, which enables solidification of nascent membranes, and solvent exchange is conducted in the No.2 coagulating bath, followed by a washing in the No.3 coagulating bath to obtain the hollow fiber membrane intermediates. Finally, membrane intermediates are winded on a fiber-collecting roller.

8. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: the multiple spinning dopes without impurity and bubbles, stated in step S2, include spinning dopes of supporting layers and separation layers, wherein, proportion of the spinning dopes for supporting layers is 80-100, and proportion of the spinning dopes for separation layers is 0-20; the spinning dopes of supporting layers include one or multitype, and the spinning dopes of separation layers include one or multitype; the bore fluid flow rate is 1-30 ml/min, and the air-gap distance is 0-40 cm.

9. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: in the stated step S2, water temperature of the coagulating baths is in the range of room temperature to 80 °C.

10. According to the preparation method of hollow fiber separation membranes with a dense-selective layer stated in Claim 1, its characteristics are that: heat-setting temperature stated in step S3 is in the range of room temperature to 120 °C, and duration lasts 0-18 hours.