membrane exhibiting high chemical resistance while having excellent separation and permeation performance has been proposed, but, among the physical properties of the membrane, properties related to the fouling of the membrane still remain unsolved.

Therefore, there is an urgent need to develop a separation membrane having excellence in anti-fouling properties against fouling materials such as organic substances, inorganic substances, and the like, antimicrobial performance against microorganisms and the like, a flux, a salt removal rate, and retention of anti-fouling properties and antimicrobial performance.

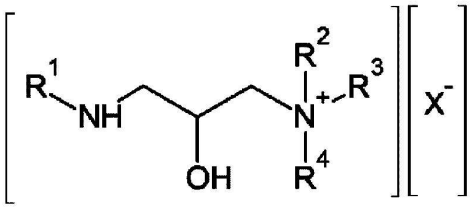
SUMMARY

The present disclosure is directed to providing a fouling resistance reverse osmosis membrane, which has excellence in anti-fouling properties against fouling materials such as organic substances, inorganic substances, and the like, antimicrobial performance against microorganisms and the like, a flux, a salt removal rate, and retention of anti-fouling properties and antimicrobial performance, a method of manufacturing the same, and a fouling resistance reverse osmosis module including the same.

One ~~aspect~~ example of the present disclosure provides a fouling resistance reverse osmosis membrane comprising: a porous support; a porous polymer support layer; a polyamide layer formed by interfacial polymerization of a first solution including a multifunctional amine compound and a second solution including a multifunctional acid halide compound; and an antimicrobial layer provided by covalent bonding of an antimicrobial agent, which is a compound represented by the

following Chemical Formula 1, to at least a portion of a surface of the polyamide layer:

[Chemical Formula 1]



in Chemical Formula 1, R^1 to R^4 each independently represent a hydrogen ion or a C_1 to C_{10} alkyl group, and X^- represents a halide ion.

According to an exemplary example of the present disclosure, the antimicrobial layer may be provided so as to entirely surround an outer surface of the polyamide layer.

In addition, the fouling resistance reverse osmosis membrane may have a flux of 24 GFD or more, a salt removal rate of 99% or more, and a flux reduction rate of less than 14%, as measured by the following Measurement Method 1.

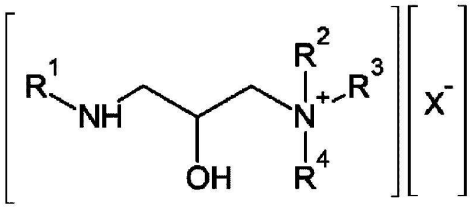
[Measurement Method 1]

A flux and a salt removal rate are measured by operating the membrane in a sodium chloride (NaCl) aqueous solution with a concentration of 2,000 ppm at 25 °C and 225 psi for an hour, and a flux reduction rate is measured by operating the membrane in the same aqueous solution in the presence of dry milk for 2 hours and then measuring a ratio of a reduced flux to an initial flux.

Another ~~aspect~~ example of the present disclosure provides a method of manufacturing a fouling resistance reverse osmosis membrane, comprising the steps of: (1) treating an upper surface of a porous support with a polymer solution to form a porous polymer support layer; (2) bringing the polymer support layer in contact with

a first solution including a multifunctional amine compound and treating the resulting polymer support layer with a second solution including a multifunctional acid halide compound to form a polyamide layer on an upper surface of the polymer support layer; and (3) treating the polyamide layer with an antimicrobial layer-forming solution containing an antimicrobial agent, which is a compound represented by the following Chemical Formula 1, to form an antimicrobial layer covalently bonded to at least a portion of a surface of the polyamide layer:

[Chemical Formula 1]



in Chemical Formula 1, R^1 to R^4 each independently represent a hydrogen ion or a C_1 to C_{10} alkyl group, and X^- represents a halide ion.

According to an exemplary example of the present disclosure, the multifunctional amine compound in the step (2) may include one or more selected from the group consisting of m-phenylenediamine, p-phenylenediamine, o-phenylenediamine, and dimethylenepiperazine.

In addition, the multifunctional acid halide compound in the step (2) may include one or more selected from the group consisting of trimesoyl chloride, isophthaloyl chloride, terephthaloyl chloride, 1,3,5-cyclohexane tricarbonyl chloride, and 1,2,3,4-cyclohexane tetracarbonyl chloride.

In addition, the covalent bonding in the step (3) may be covalent bonding of a residual functional group of the acid halide compound of the polyamide layer with the antimicrobial agent which is a compound represented by Chemical Formula 1.

In addition, the antimicrobial agent may be contained at 0.001 to 0.6 wt% with respect to the total weight of the antimicrobial layer-forming solution.

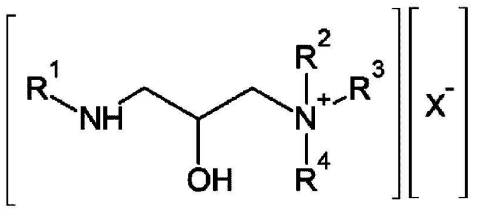
In addition, the step (3) may be performed by treatment with the antimicrobial layer-forming solution containing the antimicrobial agent at 10 to 98 °C for 5 to 600 seconds.

In addition, the polymer solution in the step (1) may include one or more polymers selected from the group consisting of a polysulfone-based polymer, a polyamide-based polymer, a polyimide-based polymer, a polyester-based polymer, an olefin-based polymer, polyvinylidene fluoride, a polybenzimidazole polymer, and polyacrylonitrile.

In addition, the polymer solution in the step (1) may include one or more solvents selected from the group consisting of N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMAc).

In one aspect, the present disclosure refers to a fouling resistance reverse osmosis membrane comprising: a porous support; a porous polymer support layer; a polyamide layer formed by interfacial polymerization of a first solution including a multifunctional amine compound and a second solution including a multifunctional acid halide compound; and an antimicrobial layer provided by covalent bonding of an antimicrobial agent, which is a compound represented by the following Chemical Formula 1, to at least a portion of a surface of the polyamide layer, wherein the antimicrobial layer is formed by treating the polyamide layer with an antimicrobial layer-forming solution, wherein the antimicrobial layer-forming solution contains the antimicrobial agent by 0.001 to 0.6 wt% with respect to a total weight of the antimicrobial layer-forming solution:

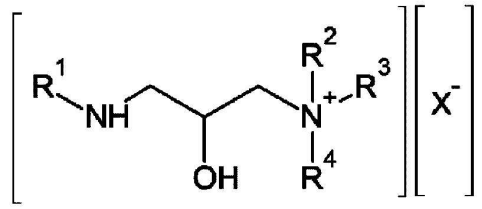
[Chemical Formula 1]



in Chemical Formula 1, R^1 to R^4 each independently represent a hydrogen ion or a C_1 to C_{10} alkyl group, and X^- represents a halide ion.

In another aspect, the present disclosure refers to a method of manufacturing a fouling resistance reverse osmosis membrane, comprising the steps of: (1) treating an upper surface of a porous support with a polymer solution to form a porous polymer support layer; (2) bringing the polymer support layer in contact with a first solution including a multifunctional amine compound and treating the resulting polymer support layer with a second solution including a multifunctional acid halide compound to form a polyamide layer on an upper surface of the polymer support layer; and (3) treating the polyamide layer with an antimicrobial layer-forming solution containing an antimicrobial agent by 0.001 to 0.6wt% with respect to a total weight of the antimicrobial layer-forming solution, which is a compound represented by the following Chemical Formula 1, to form an antimicrobial layer covalently bonded to at least a portion of a surface of the polyamide layer:

[Chemical Formula 1]



in Chemical Formula 1, R^1 to R^4 each independently represent a hydrogen ion or a C_1 to C_{10} alkyl group, and X^- represents a halide ion.

Still another aspect of the present disclosure provides a fouling resistance reverse osmosis module comprising the above-described fouling resistance reverse osmosis membrane.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

Hereinafter, the present invention will be described in detail with reference to embodiments so that those skilled in the art can easily carry out the present invention. However, the present invention may be embodied in several different forms, and therefore, is not limited to embodiments described herein.

To facilitate understanding of a fouling resistance reverse osmosis membrane according to the present invention, a fouling resistance reverse osmosis membrane of

WHAT IS CLAIMED IS:

1. A fouling resistance reverse osmosis membrane comprising:

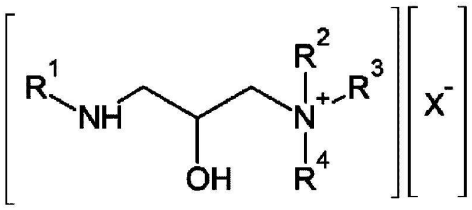
a porous support;

a porous polymer support layer;

a polyamide layer formed by interfacial polymerization of a first solution including a multifunctional amine compound and a second solution including a multifunctional acid halide compound; and

an antimicrobial layer provided by covalent bonding of an antimicrobial agent, which is a compound represented by the following Chemical Formula 1, to at least a portion of a surface of the polyamide layer, wherein the antimicrobial layer is formed by treating the polyamide layer with an antimicrobial layer-forming solution, wherein the antimicrobial layer-forming solution contains the antimicrobial agent by 0.001 to 0.6 wt% with respect to a total weight of the antimicrobial layer-forming solution:

[Chemical Formula 1]



in Chemical Formula 1, R^1 to R^4 each independently represent a hydrogen ion or a C_1 to C_{10} alkyl group, and X^- represents a halide ion.

2. The fouling resistance reverse osmosis membrane of claim 1, wherein the antimicrobial layer is provided so as to entirely surround an outer surface of the polyamide layer.

3. The fouling resistance reverse osmosis membrane of claim 1, wherein the fouling resistance reverse osmosis membrane has a flux of 24 GFD or more, a salt removal rate of 99% or more, and a flux reduction rate of less than 14%, as measured by the following Measurement Method 1.

[Measurement Method 1]

A flux and a salt removal rate are measured by operating the membrane in a sodium chloride (NaCl) aqueous solution with a concentration of 2,000 ppm at 25 °C and 225 psi for an hour, and a flux reduction rate is measured by operating the membrane in the same aqueous solution in the presence of dry milk for 2 hours and then measuring a ratio of a reduced flux to an initial flux.

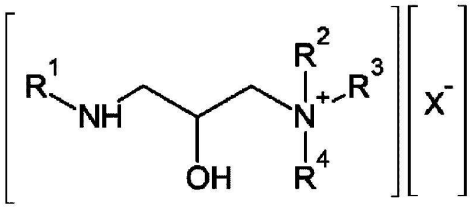
4. A method of manufacturing a fouling resistance reverse osmosis membrane, comprising the steps of:

(1) treating an upper surface of a porous support with a polymer solution to form a porous polymer support layer;

(2) bringing the polymer support layer in contact with a first solution including a multifunctional amine compound and treating the resulting polymer support layer with a second solution including a multifunctional acid halide compound to form a polyamide layer on an upper surface of the polymer support layer; and

(3) treating the polyamide layer with an antimicrobial layer-forming solution containing an antimicrobial agent by 0.001 to 0.6wt% with respect to a total weight of the antimicrobial layer-forming solution, which is a compound represented by the following Chemical Formula 1, to form an antimicrobial layer covalently bonded to at least a portion of a surface of the polyamide layer:

[Chemical Formula 1]



in Chemical Formula 1, R^1 to R^4 each independently represent a hydrogen ion or a C_1 to C_{10} alkyl group, and X^- represents a halide ion.

5. The method of claim 4, wherein the multifunctional amine compound in the step (2) includes one or more selected from the group consisting of m-phenylenediamine, p-phenylenediamine, o-phenylenediamine, and dimethylenepiperazine.

6. The method of claim 4, wherein the multifunctional acid halide compound in the step (2) includes one or more selected from the group consisting of trimesoyl chloride, isophthaloyl chloride, terephthaloyl chloride, 1,3,5-cyclohexane tricarbonyl chloride, and 1,2,3,4-cyclohexane tetracarbonyl chloride.

7. The method of claim 4, wherein the covalent bonding in the step (3) is covalent bonding of a residual functional group of the acid halide compound of the

polyamide layer with the antimicrobial agent which is a compound represented by Chemical Formula 1.

~~8. The method of claim 4, wherein the antimicrobial agent is contained at 0.001 to 0.6 wt% with respect to a total weight of the antimicrobial layer forming solution.~~

~~9~~8. The method of claim 4, wherein the step (3) is performed by treatment with the antimicrobial layer-forming solution containing the antimicrobial agent at 10 to 98 °C for 5 to 600 seconds.

~~10~~9. The method of claim 4, wherein the polymer solution in the step (1) includes one or more polymers selected from the group consisting of a polysulfone-based polymer, a polyamide-based polymer, a polyimide-based polymer, a polyester-based polymer, an olefin-based polymer, polyvinylidene fluoride, a polybenzimidazole polymer, and polyacrylonitrile.

1~~1~~0. The method of claim 4, wherein the polymer solution in the step (1) includes one or more solvents selected from the group consisting of N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMAc).

1~~2~~1. A fouling resistance reverse osmosis module comprising the fouling resistance reverse osmosis membrane according to any one of claim 1 to claim 3.