

REJECTION IMPROVER OF REVERSE OSMOSIS MEMBRANE, METHOD FOR
IMPROVING REJECTION, AND REVERSE OSMOSIS MEMBRANE

Field of Invention

[0001]

The present invention relates to a rejection improver which exerts a high rejection improving effect with respect to a reverse osmosis (RO) membrane, particularly an aromatic polyamide base RO membrane, without reducing an amount of permeate water significantly, where the rejection (salt rejection) of the RO film has been degraded in the process of use thereof. In particular, in consideration of the fact that the permeate water of an RO membrane is used as drinking water and domestic water and concentrated water is discharged into an environment, the present invention relates to a rejection improver of an RO membrane which is safe even in the case of leakage to the permeate water side in the process of improvement of the rejection of the RO membrane and which does not apply a heavy load on the environment even in the case of discharge to the concentration side.

Also, the present invention relates to a method for improving the rejection of an RO membrane by using this rejection improver and an RO membrane subjected to a rejection improving treatment with this rejection improver.

Background of Invention

[0002]

At present, in order to make up for a global shortage of water supply, desalination of seawater saltwater and water recovery are performed using an RO membrane system. In the RO membrane system, in a pretreatment step, an oxidizing agent, e.g., chlorine (sodium hypochlorite or the like) or hydrogen peroxide, is added to raw water (water to be treated with RO membrane, hereafter may be referred to as "RO feed water") to suppress biofouling.

However, these oxidizing agents have a strong oxidative decomposition effect. Therefore, it is known that if these oxidizing agents are added and, thereafter, raw water is fed to an RO membrane while a reduction treatment is insufficient, the RO membrane is degraded.

Meanwhile, in many cases, a reducing agent, e.g., sodium bisulfite, is added to the raw water to decompose an oxidizing agent in the raw water and, thereafter, the raw water is fed to the RO membrane. However, it is also known that, in a reducing environment, in which sodium bisulfite is excessively added, if a metal, e.g., Cu or Co, is present together in the raw water, the RO membrane is degraded and the rejection is reduced (Patent Document 1, Non-Patent Document 1).

[0003]

The following methods for improving the rejection of an RO membrane have been proposed previously. However, the individual methods have respective problems, and improvements thereof have been desired.

[0004]

i) A method improving the rejection of an RO membrane by adhering an anionic or cationic high-molecular compound to the membrane surface (Patent Document 2).

This method has especially an effect of improving the rejection of an electrolyte with respect to an RO membrane degraded to a small extent or an unused RO membrane, but the effect is low with respect to an improvement of rejection of a nonelectrolyte and an improvement of rejection of an RO membrane degraded to a large extent.

[0005]

ii) A method improving the rejection of an RO membrane by adhering a compound having a polyalkylene glycol chain to the membrane surface (Patent Document 3).

This method has an effect of improving the rejection of a nonelectrolyte as well, but the effect may be low with respect to an improvement of rejection of an RO membrane degraded to a large extent. In addition, there is a problem in decrease in permeate flux. The permeate flux may be decreased by 20% or more as compared with that of the unused RO membrane.

[0006]

iii) A method in which a nonionic surfactant is adsorbed to an RO membrane (Patent Document 4).

There are nonionic surfactants having a polyalkylene glycol chain, and this case is included in Patent Document 3. The surfactant has a hydrophobic group as an intrinsic

property of the surfactant, and this is adsorbed by the RO membrane, so that the permeate flux decreases significantly.
[0007]

iv) A method in which the salt rejection is improved by adhering tannic acid or the like to an RO membrane (Non-Patent Document 2).

The rejection improving effect of this method is not large. For example, even when the salt rejection of degraded ES20 (produced by NITTO DENKO CORPORATION) and SUL-G20F (produced by Toray Industries, Ltd.), which are RO membranes, are improved by the method concerned, the solute concentration of the permeate water of the membrane after being improved cannot become one-half or less of the solute concentration of the permeate water of the membrane before being improved.

[0008]

v) A method in which the rejection of an RO membrane is improved by adding tannic acid and a polymer (polyvinyl methyl ether) in combination (Non-Patent Document 3).

It is believed that the effect of this method is improved as compared with the effect of the method by using only tannic acid. However, the permeate flux decreases by about 20% in average, and as for the rejection improving effect thereof, the solute concentration of the permeate water cannot become one-half or less in some cases, for example, the salt rejection of an RO membrane, the salt rejection of which has decreased to 90.5%, is made to be

92.5%.

[0009]

Meanwhile, it is known that when an RO membrane is oxidized and degraded by a chlorine base oxidizing agent, a carboxyl group is generated (Non-Patent Documents 4 and 5). The present inventors found that carboxyl groups were present on the surface of even a virgin aromatic polyamide base RO membrane, and carboxyl groups increased even when the membrane was degraded because of the factors, e.g., alkali and hydrogen peroxide, other than chlorine base oxidizing agent. Here, the carboxyl group can be detected by an XPS method in which the detection sensitivity of the carboxyl group is enhanced by performing surface modification.

[0010]

vi) On the basis of the finding that carboxyl groups are present in the RO membrane and the carboxyl group increases by degradation, the present inventors found a method for improving the rejection of an RO membrane by using a compound having an amino group and inducing bonding to a carboxyl group (Patent Documents 5 and 6). The basic technical ideas of these Patent Documents 5 and 6 reside in that many carboxyl groups are present in a portion degraded significantly and, therefore, a compound having a molecular weight of 1,000 or less and having an amino group is allowed to adsorb to that portion concentratedly.

[0011]

In addition, the present inventors found that adsorption of a low molecular compound to an RO membrane was indispensable for improving the rejection of the RO membrane (Patent Document 7).

That is, the isopropyl alcohol (IPA) rejection of the aromatic polyamide base RO membrane is 80% to 95%. The molecular weight of IPA is 60 and, therefore, it can be considered that the molecular weight cutoff of the RO membrane with respect to the nonelectrolyte is about 60. When it is considered that a decrease in rejection of the RO membrane is because of an expansion of gaps of the dense layer of the RO membrane, it is considered to be desirable to fill the expanded gaps of the dense layer of the RO membrane with a substance slightly larger than the molecular weight cutoff. In this regard, it is considered that gaps have various sizes and, therefore, it is also considered to be more desirable to use substances having a plurality of molecular weights. It is considered that fixation of low molecule proceeds by finally using a substance having a molecular weight relatively larger than those low molecules.

[0012]

This method for improving the rejection of an RO membrane according to Patent Document 7 is a method in which an aqueous solution containing a first organic compound having a molecular weight of less than 200, a second organic compound having a molecular weight of 200 or more and less than 500, and a third organic compound having a molecular

weight of 500 or more is passed through a reverse osmosis membrane. The first and second organic compounds are preferably an amino acid or an amino acid derivative. Meanwhile, as for the third organic compound, functional groups which act on a carboxyl group of the membrane (cationic group: primary to quaternary amino groups), compounds which act on the compounds having an amino group in a rejection improver (anionic group: carboxyl group, sulfonic group, hydroxyl group of aromatic (phenolic hydroxyl group)), compounds having functional groups (hydroxyl group) which acts on a polyamide membrane, or compounds having a cyclic structure can be used.

[0013]

The mechanism of repair of a degraded membrane according to Patent Document 7 will be described below with reference to Figs. 1 and 2.

[0014]

A normal amide bond of an RO membrane, for example, an aromatic polyamide base RO membrane, takes on a structure indicated as a normal membrane shown in Fig. 1. In the case where this membrane is degraded by an oxidizing agent, e.g., chlorine, a C-N bond of the amide bond is cut, and finally a structure indicated by a degraded membrane shown in Fig. 1 is taken on.

[0015]

As indicated by the degraded membrane shown in Fig. 1, the amino group may disappear by cutting of the amide bond,

and a carboxyl group is formed in at least part of this cut portion.

[0016]

As degradation proceeds, gaps of the dense layer of the RO membrane are expanded and various sizes of gaps are formed. The first to third organic compounds A to C having different molecular weights (the order of the molecular weights is organic compound A < organic compound B < organic compound C) are fixed to the above-described RO membrane in accordance with the sizes of the gaps, as shown in Fig. 2. Consequently, the individual holes (gaps of the dense layer) having various sizes of the degraded membrane are repaired and the rejection of the membrane is recovered.

[0017]

According to Patent Document 7, the aqueous solution containing a plurality of amino compounds (the first and second organic compounds) having different molecular weights and skeletons (structures) are allowed to permeate the degraded membrane, the individual compounds become barriers to each other when permeating the membrane, a residence time in a degraded portion in the membrane increases and, thereby, the probability of contact between the carboxyl group in the membrane and the amino group in the low-molecular-weight amino compound increases, so that the efficiency of repair of the membrane is improved. Furthermore, a large degraded portion of the membrane can be blocked by using a third organic compound having a molecular weight of 500 or more in

combination and, thereby, the efficiency of repair is still more enhanced.

Citation List

[0018]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 7-308671

Patent Document 2: Japanese Unexamined Patent Application Publication No. 2006-110520

Patent Document 3: Japanese Unexamined Patent Application Publication No. 2007-289922

Patent Document 4: Japanese Unexamined Patent Application Publication No. 2008-86945

Patent Document 5: International Publication No. WO 2011/040354A1 pamphlet

Patent Document 6: Japanese Patent Application No. 2011-051525 (Japanese Unexamined Patent Application Publication No. 2012-187468)

Patent Document 7: Japanese Patent Application No. 2011-051530 (Japanese Unexamined Patent Application Publication No. 2012-187469)

[0019]

Non-Patent Document 1: Nagai et al. Desalination, Vol. 96 (1994), 291-301

Non-Patent Document 2: Sato and Tamura, KAGAKU KOGAKU RONBUNSHU, Vol. 34 (2008), 493-498

Non-Patent Document 3: S.T. Mitrouli, A.J. Karabelas, N.P. Isaias, D.C. Sioutopoulos, and A.S. Al Rammah, Reverse

Osmosis Membrane Treatment Improves Salt-Rejection

Performance, IDA Journal I Second Quarter 2010, p22-34

Non-Patent Document 4: Uemura et al. Bulletin of the Society of Sea Water Science, Japan, 57, 498-507 (2003)

Non-Patent Document 5: Yoshiyasu Kamiyama, Hyoumen, vol. 31, No. 5 (1993), 408-418

Object and Summary of Invention

[0020]

The rejection of the RO membrane can be effectively improved by the rejection improving method according to Patent Document 7. However, there are problems in that when a plurality of organic compounds having different molecular weights are mixed and dissolved into an aqueous solution, aggregates are generated, so as to adhere to a chemical solution tank, cause obstruction of flow paths of a membrane module, degrade the effect of the chemical agent, and the like. Also, there are problems in that, for example, part of organic compounds have low solubility in water and are not dissolved easily. Also, when organic compounds having an amide bond and an ester bond are preserved in the state of an aqueous solution, hydrolysis may occur and degradation in the chemical agent may occur. Furthermore, in storage as an aqueous solution, there are a problem in generation of precipitation due to a decrease in a storage temperature and a problem in microbial propagation due to an increase in a storage temperature.

[0021]

The present invention has been made in consideration of these problems. An object of the present invention is to provide a technology to prevent generation of aggregates, poor dissolution into water, hydrolysis, and the like of an RO membrane rejection improver containing at least two types of organic compounds having different molecular weights and use the rejection improver effectively for a treatment to improve the rejection of an RO membrane.

[0022]

The present inventors performed intensive studies over and over again to solve the above-described issue and obtained following findings.

[0023]

1) Among the plurality of types of organic compounds used for the rejection improver, for example, if an organic compound, which exhibits a pH of an aqueous solution of 7 or more when being dissolve into water alone, and an organic solution, which exhibits a pH of less than 7, are mixed and dissolved into water at high concentrations, aggregates may be generated. Basically, an organic compound exhibiting a pH of 7 or more is alkaline and an organic compound exhibiting a pH of less than 7 is acid. It can be said that an organic compound having an amino group is a weakly alkaline substance. Meanwhile, in the case where an organic compound used in combination with this is weakly acid or has a large molecular weight, when these are made into a high concentration aqueous solution, an insoluble salt is

generated, and this becomes aggregates. Therefore, in the case where at least two types of organic compounds are contained in the rejection improver, it is necessary to separate into two parts at the stage before dissolution, i.e. at the stage of a powder, in order that aggregation does not occur in dissolution at high concentrations. For example, when arginine and tannic acid are dissolved into water in such a way that each concentration becomes 1 percent by weight, aggregates are generated and, therefore, it is necessary that a powder containing arginine and a powder containing tannic acid are separated.

[0024]

2) Aspartame is a substance produced by an amide bond between a methyl ester of phenylalanine and aspartic acid, and the solubility in water is low, whereas the solubility in an alkaline aqueous solution increases. Consequently, this substance is mixed with arginine or the like, which exhibits a pH of 7 or more when being dissolved into water, so as to produce a mixed powder, aqueous solution is prepared by using the resulting mixed powder and, thereby, the solubility can be increased when an aqueous solution is produced. Meanwhile, aspartame has a property of being hydrolyzed when being preserved for a long period under an alkaline condition, although denaturing due to hydrolysis can be suppressed by storage in the state of a powder. Here, arginine is an organic compound. However, the pH after dissolution may be adjusted by an inorganic compound, e.g.,

a carbonate or a phosphate.

[0025]

3) In the case where a treatment to improve the rejection of an RO membrane is performed by using a powdered chemical agent separated into two parts, dissolution into water up to an actual use concentration of 0.1 to 1000 mg/L in one stroke is not effective to obtain a homogeneous aqueous solution. Meanwhile, if two organic compounds in a high concentration state come into contact with each other, there is a risk of generation of aggregates. Consequently, it is preferable that these two powdered chemical agents be independently dissolved once to become 1 to 200 g/L and, thereafter, be made into a diluted aqueous solution. In this regard, the substances having an amide bond or an ester bond may be hydrolyzed under the alkaline condition or acid condition, as described above. Therefore, after dissolution into water, it is necessary that dilution to a use concentration is performed as soon as possible, so as to use for the treatment to improve the rejection of an RO membrane. Then, the two powdered chemical agents independently dissolved once in such a way that each organic compound concentration becomes 1 to 200 g/L are used after being diluted to have a concentration of 0.1 to 1000 mg/L in the next step. In the case of this aqueous solution having an organic compound concentration of 0.1 to 1000 mg/L, even when all the organic compounds are present in the same aqueous solution, the estimated concentration of generated

salt becomes less than or equal to the solubility, so that aggregates are not generated. Therefore, the aqueous solution in which all the organic compounds are dissolved can be used for the treatment to improve the rejection of the RO membrane. Alternatively, as another method, aqueous solutions, in which the two powdered chemical agents are independently dissolved in such a way that each organic compound concentration becomes 1 to 200 g/L, can be line-injected so as to be diluted and mixed in a line.

Alternatively, it is also possible to adopt a method in which after the two powdered chemical agents are independently dissolved in such a way that each organic compound concentration becomes 1 to 200 g/L, dilution is performed in such a way that each organic compound concentration after mixing becomes 0.1 to 1000 mg/L, and contact with the RO membrane is performed separately.

[0026]

The present invention has been achieved on the basis of the above-described findings and the gist is as described below.

[0027]

[1] A rejection improver of a reverse osmosis membrane, characterized by containing at least two types of organic compounds having different molecular weights, wherein the rejection improver of a reverse osmosis membrane contains at least an organic compound, which has a molecular weight of 60 or more and less than 500 and which has an amino group,

and tannic acid, and the above-described organic compound having an amino group and the above-described tannic acid are stored as two powdered chemical agents different from each other.

[0028]

[2] The rejection improver of a reverse osmosis membrane, according to the item [1], characterized in that when the above-described two powdered chemical agents are made into their respective aqueous solutions having each organic compound concentration of 1 to 200 g/L, the pH of an aqueous solution of one powdered chemical agent containing the above-described organic compound having an amino group is 7 or more, and the pH of an aqueous solution of the other powdered chemical agent containing the above-described tannic acid is less than 7.

[0029]

[3] A method for improving the rejection of a reverse osmosis membrane by treating the reverse osmosis membrane through the use of an aqueous solution of the rejection improver according to the item [1] or item [2], the method characterized by including the steps of preparing an aqueous solution having an organic compound concentration (in the case where the powdered chemical agent contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L by dissolving at least one powdered chemical agent of the above-described two powdered chemical agents

into water and diluting the aqueous solution in such a way that the organic compound concentration (in the case where the powdered chemical agent contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of the aqueous solution becomes 0.1 to 1000 mg/L.

[0030]

[4] A method for improving the rejection of a reverse osmosis membrane by treating the reverse osmosis membrane through the use of an aqueous solution of the rejection improver according to the item [1] or item [2], the method characterized by including the step of preparing an aqueous solution having each organic compound concentration of 1 to 1000 mg/L by dissolving the above-described two powdered chemical agents into water independently and mixing the resulting aqueous solutions.

[0031]

[5] A method for improving the rejection of a reverse osmosis membrane by treating the reverse osmosis membrane through the use of an aqueous solution of the rejection improver according to the item [1] or item [2], the method characterized by including the step of diluting and mixing aqueous solutions, which are obtained by dissolving the above-described two powdered chemical agents into water independently, by line-injecting them from mutually independent positions.

[0032]

[6] A reverse osmosis membrane subjected to a rejection improving treatment through the use of the rejection improver according to the item [1] or item [2].

[0033]

[7] A reverse osmosis membrane subjected to a rejection improving treatment by the method for improving the rejection according to any one of the items [3] to [5].

Advantageous Effects of Invention

[0034]

According to the present invention, the following effects and advantages are offered, generation of aggregates, poor dissolution into water, hydrolysis, and the like of an RO membrane rejection improver containing at least two types of organic compounds having different molecular weights are prevented, and the rejection improver is used effectively for a treatment to improve the rejection of an RO membrane, so that an effective treatment to improve the rejection of the RO membrane can be performed.

[0035]

i) In preparation of an aqueous solution by separating an organic compound having an amino group and tannic acid, which may produce aggregates when being mixed at high concentrations and which are constituents of the rejection improver, into two powders and dissolving them into water, generation of aggregates can be suppressed by initially, performing dissolution individually in such a way that the concentration becomes 1 to 200 g/L on each organic compound

concentration basis, and furthermore, diluting and mixing them in such a way that the concentration becomes 0.1 to 1000 mg/L on each organic compound concentration basis. Consequently, the above-described problems due to aggregates can be avoided.

[0036]

ii) It becomes possible to prepare an aqueous solution having a concentration of 1 to 200 g/L easily by mixing a constituent of the rejection improver, such as, the organic compound having an amino group which is not dissolved easily at usual pH, with a substance which exhibits alkalinity or acidity when being dissolved.

[0037]

iii) Hydrolysis can be suppressed by storing a constituent, which has an amide bond or an ester bond and which is susceptible to hydrolysis in an aqueous solution, of the rejection improver in the state of a powder, and degradation in chemical agent effect due to hydrolysis can be prevented.

[0038]

iv) Storage is performed as a powder and, therefore, problems in the case where storage is performed as an aqueous solution, for example, generation of precipitation due to a decrease in temperature and microbial propagation due to an increase in temperature, can be avoided. This is particularly effective in the case where the organic compound is a food additive.

Brief Description of Drawings

[0039]

Fig. 1 is an explanatory diagram of chemical structural formulae indicating a normal membrane and a degraded membrane.

Fig. 2 is an explanatory diagram of a chemical structural formula showing the mechanism of a rejection improving treatment according to Patent Document 7.

Fig. 3 is a schematic diagram showing a flat sheet membrane tester used in an example.

Description of Embodiments

[0040]

The embodiments according to the present invention will be described below in detail.

[0041]

[Rejection improver]

A rejection improver of an RO membrane, according to the present invention, is a rejection improver, which contains at least two types of organic compounds having different molecular weights, of a reverse osmosis membrane, and is characterized by containing at least an organic compound, which has a molecular weight of 60 or more and less than 500 and which has an amino group, and tannic acid as the at least two types of organic compounds and being stored as two powdered chemical agents containing organic compounds different from each other.

[0042]

Examples of organic compound, which has a molecular weight of 60 or more and less than 500 and which has an amino group, (hereafter may be referred to as a "low-molecular-weight amino compound") serving as a constituent of the rejection improver according to the present invention includes the compounds as described below.

[0043]

Aromatic amino compounds: for example, compounds having a benzene skeleton and an amino group, e.g., aniline (molecular weight 93) and diaminobenzene (molecular weight 108)

[0044]

Aromatic aminocarboxylic acid compounds: for example, compounds having a benzene skeleton, at least two amino groups, and carboxyl groups, the number of which is smaller than the number of amino groups, e.g., 3,5-diaminobenzoic acid (molecular weight 152), 3,4-diaminobenzoic acid (molecular weight 152), 2,4-diaminobenzoic acid (molecular weight 152), 2,5-diaminobenzoic acid (molecular weight 152), and 2,4,6-triaminobenzoic acid (molecular weight 167)

[0045]

Aliphatic amino compounds: for example, compounds having a straight chain hydrocarbon group having the carbon number of about 1 to 20 and at least one amino group, e.g., methylamine (molecular weight 31), ethylamine (molecular weight 45), octylamine (molecular weight 129), and 1,9-diaminononane (may be abbreviated as "NMDA" in the present

specification) ($\text{C}_9\text{H}_{18}(\text{NH}_2)_2$) (molecular weight 158) and compounds having a branched hydrocarbon group having the carbon number of about 1 to 20 and at least one amino group, e.g., 1-aminopentane (may be abbreviated as "IAAM" in the present specification) ($\text{NH}_2(\text{CH}_2)_4\text{CH}_3$) (molecular weight 87) and 2-methyl-1,8-octanediamine (may be abbreviated as "MODA" in the present specification) ($\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{NH}_2$) (molecular weight 158).

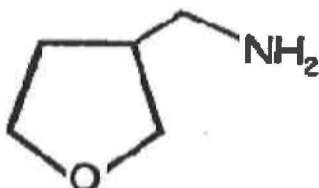
[0046]

Aliphatic aminoalcohols: compounds having a straight chain or branched hydrocarbon group having the carbon number of 1 to 20, an amino group, and a hydroxy group, e.g., 4-amino-2-methyl-1-butanol (may be abbreviated as "AMB" in the present specification) ($\text{NH}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$) (molecular weight 103).

[0047]

Alicyclic amino compounds: compounds having an alicyclic ring and an amino group, e.g., tetrahydrofurfurylamine (may be abbreviated as "FAM" in the present specification) (the following structural formula) (molecular weight 101).

[0048]



[0049]

Amino acid compounds: for example, basic amino acid compounds, e.g., arginine (molecular weight 174) and ricin (molecular weight 146), amino acid compounds having an amide group, e.g., asparagine (molecular weight 132) and glutamine (molecular weight 146), and other amino acid compounds, e.g., glycine (molecular weight 75) and phenylalanine (molecular weight 165).

[0050]

One type of these low-molecular-weight amino compounds may be used alone or at least two types may be used in combination. In the present invention, it is preferable that among these low-molecular-weight amino compounds, a first low-molecular-weight amino compound having a molecular weight of less than 200 and a second low-molecular-weight amino compound having a molecular weight of 200 or more and less than 500 be used in combination. In this case, amino acids or amino acid compounds are suitable for the first low-molecular-weight amino compound and, for example, arginine (molecular weight 174), ricin (molecular weight 146), and histidine (molecular weight 155), which are basic amino compounds, and glycine (molecular weight 75) having smaller molecular weight are preferable. As for the second low-molecular-weight amino compound, peptide or derivatives thereof, for example, aspartame (molecular weight 294) which is a methyl ester of dipeptide of phenylalanine and aspartic acid is suitable.

[0051]

In general, the amino acid has high solubility in water, where the resulting aqueous solution is stable, reacts with a carboxyl group of a membrane so as to be bonded to the RO membrane, forms an insoluble salt so as to block holes generated because of degradation of the membrane and, thereby, enhances the rejection of the membrane.

[0052]

One type of these low-molecular-weight amino compounds may be used alone or at least two types may be used in combination. In the case where an aqueous solution containing at least two types of low-molecular-weight amino compounds having different molecular weights and skeleton structures are allowed to permeate the RO membrane, the individual compounds become barriers to each other when permeating the membrane, a residence time in a degraded portion in the membrane increases and, thereby, the probability of contact between the carboxyl group in the membrane and the amino group in the low-molecular-weight amino compound increases, so that the efficiency of repair of the membrane is improved.

[0053]

Furthermore, a large degraded portion of the membrane can be blocked by using tannic acid having a molecular weight of 500 or more in combination with these low-molecular-weight amino compounds and, thereby, the efficiency of repair is enhanced.

[0054]

In the present invention, the above-described low-molecular-weight amino compound and tannic acid are stored in such a way that they become two powdered chemical agents different from each other. It is preferable that these two powdered chemical agents form a combination of an aqueous solution, the pH of which is 7 or more, of one powdered chemical agent containing the organic compound having an amino group and an aqueous solution, the pH of which is less than 7, of the other powdered chemical agent containing tannic acid, where each powdered chemical agent is used and is made into an aqueous solution having a concentration of each organic compound contained in the powdered chemical agent concerned of 1 to 200 g/L.

In this manner, the organic compound which becomes alkaline aqueous solution having a pH of 7 or more and the organic compound which becomes acid aqueous solution having a pH of less than 7 are stored as different powdered chemical agents, and aqueous solutions are prepared individually, so that generation of aggregates because of reaction between them can be prevented.

[0055]

As described above, aspartame has relatively high solubility in an alkaline aqueous solution. Therefore, it is preferable that aspartame be mixed with a low-molecular-weight amino compound, e.g., arginine, which becomes alkaline aqueous solution having a pH of 7 or more when being dissolved into water, so as to become a powdered

chemical agent, and the resulting mixed powder be dissolved into water, so as to prepare an aqueous solution. In this regard, when the low-molecular-weight amino compound is dissolved into water, the pH may be adjusted in such a way as to enhance the solubility by using an inorganic compound, e.g., a carbonates or a phosphate, as a pH regulator. For that purpose, a powdered chemical agent may be prepared by mixing these pH regulators with the low-molecular-weight amino compound in advance.

In the rejection improver according to the present invention, the contents of at least two types of organic compounds in the powdered chemical agent containing the at least two types of organic compounds may be tailored to the contents in the powdered chemical agent in accordance with the proportions in the use in such a way that suitable proportions in use is ensured in the use as a rejection improver.

[0056]

[Method for improving rejection]

The method for improving the rejection of the RO membrane according to the present invention is to perform an RO membrane rejection improving treatment through the use of the rejection improver according to the present invention made from the above-described two powdered chemical agents. Specifically, the rejection of a degraded RO membrane is improved by passing the aqueous solution of the rejection improver according to the present invention through the RO

membrane. Hereafter the rejection improver aqueous solution to be passed through the RO membrane for the RO membrane rejection improving treatment is referred to as "rejection improving treatment water".

[0057]

In the method for improving the rejection of the RO membrane according to the present invention, each of concentrations of the above-described low-molecular-weight amino compound and tannic acid, which are constituents of the rejection improver in the rejection improving treatment water, is preferably 1 to 1000 mg/L, more preferably 1 to 800 mg/L, yet more preferably 1 to 200 mg/L, and further more preferably 1 to 100 mg/L. If the concentration of each component in the rejection improving treatment water is lower than the above-described lower limit, sufficient rejection improving effect cannot be obtained, and if the concentration is higher than the above-described upper limit, aggregates may be generated.

[0058]

As described above, when the RO membrane rejection improving treatment is performed through the use of the rejection improver according to the present invention, it is not preferable to directly prepare the above-described rejection improving treatment water having a low concentration by using the two powdered chemical agents serving as the rejection improver according to the present invention because homogeneous aqueous solution cannot be

obtained in some cases.

Therefore, preferably, the two powdered chemical agents are used, initially high-concentration aqueous solutions having each organic compound concentration of 1 to 200 g/L are prepared, and then, dilution and mixing are performed by using them in such a way that an aqueous solution having each organic compound concentration of 1 to 1000 mg/L is passed through the RO membrane.

[0059]

Consequently, in the case of a rejection improver made from, for example, Powdered chemical agent A and Powdered chemical agent B, it is preferable that dissolution into water, mixing, and dilution be performed by adopting the following mode I, II, or III.

[0060]

I: Powdered chemical agent A is used and an aqueous solution having an organic compound concentration (in the case where Powdered chemical agent A contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L is prepared. On the other hand, Powdered chemical agent B is used and an aqueous solution having an organic compound concentration (in the case where Powdered chemical agent B contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L is prepared. These aqueous solutions are diluted and mixed, so

as to prepare a rejection improving treatment water having a concentration of each organic compound of 0.1 to 1000 mg/L.

II: Powdered chemical agent A is used and an aqueous solution having an organic compound concentration (in the case where Powdered chemical agent A contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L is prepared. On the other hand, Powdered chemical agent B is used and an aqueous solution having an organic compound concentration (in the case where Powdered chemical agent B contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L is prepared. These aqueous solutions are diluted individually and diluted aqueous solutions are mixed, so as to prepare a rejection improving treatment water having a concentration of each organic compound of 0.1 to 1000 mg/L.

III: Powdered chemical agent A is used and an aqueous solution having an organic compound concentration (in the case where Powdered chemical agent A contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L is prepared. On the other hand, Powdered chemical agent B is used and an aqueous solution having an organic compound concentration (in the case where Powdered chemical agent B contains at least two types of organic compounds, this organic compound concentration refers to

each organic compound concentration) of 1 to 200 g/L is prepared. These aqueous solutions are line-injected into a feed pipe of an RO feed water from mutually independent positions, so as to prepare a rejection improving treatment water having a concentration of each organic compound of 0.1 to 1000 mg/L.

[0061]

In this regard, the ratio $C_{\min}/C_{\max}$ of the concentration $C_{\min}$ of an organic compound having the lowest concentration among the organic compounds in the rejection improving treatment water to the concentration $C_{\max}$ of an organic compound having the highest concentration is preferably 0.1 to 1.0. If this value is less than 0.1, bias may occur in the sizes of repairable holes. All concentrations of organic compounds may be equal.

[0062]

Meanwhile, inorganic electrolytes, e.g., a common salt (NaCl), neutral organic matters, e.g., isopropyl alcohol and glucose, a low molecular polymer, e.g., polymaleic acid, and the like may be added as a tracer to the rejection improving treatment water. Consequently, the degree of permeation of a common salt or glucose into permeate water of the reverse osmosis membrane is analyzed and, thereby, the degree of repair of the membrane can be examined.

[0063]

Preferably, the feed water pressure when the rejection improving treatment water is passed through the RO membrane

is specified to be 20% to 150%, particularly 50% to 130% of the normal operation pressure of the RO membrane concerned because if the pressure is too high, there is a problem in that adsorption to portions not degraded proceeds and if the pressure is too low, adsorption to even portions degraded does not proceed. In the case where the membrane of the RO membrane is an ultra-low pressure membrane, the inlet pressure of the apparatus is preferably 0.1 to 1.0 MPa. In the case where the membrane of the RO membrane is a low-pressure membrane, the inlet pressure of the apparatus is preferably 0.1 to 2.0 MPa. In the case where the membrane of the RO membrane is a seawater desalination membrane, the inlet pressure of the apparatus is preferably 0.1 to 7.0 MPa. [0064]

Meanwhile, in the present invention, preferably, the rejection improving treatment water is allowed to pass through, that is, permeate the RO membrane in such a way that the minimum amount of contact of organic compound per unit area of membrane calculated from the following formula becomes 2,500 mg/m² or more, preferably 2,500 to 1,000,000 mg/m², particularly preferably 3,000 to 100,000 mg/m².

minimum amount of contact of organic compound (mg/m²) =
[minimum organic compound concentration (mg/L) × treatment
time (hr) × amount of permeate water in treatment
(m³/hr)/membrane area (m²)] × 1000

Here, the minimum organic compound concentration refers to the concentration of an organic compound having the

lowest concentration among the organic compounds in the rejection improving treatment water.

[0065]

The minimum amount of contact of organic compound is specified to be as described above and, thereby, the rejection of the RO membrane is improved sufficiently. For example, in the case where two types of the above-described low-molecular-weight amino compounds are used, the concentration of the first low-molecular-weight amino compound in the rejection improving treatment water is specified to be C_1 (mg/L), the concentration of the second low-molecular-weight amino compound in the rejection improving treatment water is specified to be C_2 (mg/L), the concentration of tannic acid in the rejection improving treatment water is specified to be C_3 (mg/L), and the lowest concentration among C_1 to C_3 is specified to be $C_{\min}$, the minimum amount of contact of organic compound per unit area of membrane is calculated by the following formula.

minimum amount of contact of organic compound per unit area of membrane = $[(C_{\min}) \times \text{treatment time (Hr)} \times \text{amount of permeate water in treatment (m}^3/\text{Hr)}/\text{membrane area (m}^2)] \times 1000$

[0066]

In the method according to the present invention, the linear velocity of the RO membrane permeate water during the rejection improving treatment is preferably 0.1 to 5 m/d, although depending on the pressure, the water temperature,

the shape of membrane, and the like. This is because if the velocity is too high, there is a problem in that adsorption to portions not degraded proceeds and if the velocity is too low, the contact efficiency with portions degraded is degraded as with the above description.

[0067]

Meanwhile, the water temperature of the rejection improving treatment water during the rejection improving treatment is preferably ambient temperature, for example, about 10°C to 35°C. If the water temperature is too low, the amount of permeate water decreases and the contact efficiency is degraded. If the temperature of the rejection improving treatment water is too high, a membrane material may be denatured.

[0068]

Preferably, the duration of passing through of the rejection improving treatment water is specified to be the duration in which each organic compound permeates the RO membrane sufficiently. In the case where the rejection improving treatment water is passed through when an RO membrane apparatus is not at a steady operation, it is preferable that the water be passed for about 3 to 100 hours, and particularly about 6 to 50 hours. If the duration of passing of the water is too short, the treatment is finished while the organic compound is not fixed sufficiently, so that adhered organic compounds may be peeled off.

[0069]

The rejection improving treatment may be performed at a steady operation of the RO membrane apparatus and may be performed by, for example, adding an aqueous solution prepared from the rejection improving treatment agent to the RO feed water at a steady operation of the RO membrane apparatus. The duration of addition of an aqueous solution of the rejection improving treatment agent to the RO feed water is favorably about 1 to 500 hours. However, the aqueous solution of the rejection improving treatment agent may be added to the RO feed water constantly.

[0070]

In the case where the RO membrane apparatus has been operated for a long time and, thereby, pollution of the membrane have occurred so as to reduce the permeate flux, the rejection improving treatment may be performed after the membrane is cleaned.

[0071]

Examples of membrane cleaning agents used in this case can include mineral acids, e.g., hydrochloric acid, nitric acid, and sulfuric acid, and organic acids, e.g., citric acid and oxalic acid, for acid cleaning. As for alkali cleaning, sodium hydroxide, potassium hydroxide, and the like can be mentioned. In general, the pH is specified to be about 2 for acid cleaning and the pH is specified to be about 12 for alkali cleaning.

[0072]

[RO membrane]

In the present invention, examples of membrane structures of the RO membrane to be treated by the rejection improving treatment can include polymer membranes, e.g., asymmetric membranes and composite membranes. Examples of materials for the RO membrane can include polyamide base materials, e.g., aromatic polyamides, aliphatic polyamides, and composite materials thereof, and cellulose base materials, e.g., cellulose acetate. The rejection improver and the rejection improving method according to the present invention can be particularly favorably applied to the RO membranes which are RO membranes made from aromatic polyamide base materials, among the above-described materials, and which have many carboxyl groups because of cutting of C-N bond due to degradation. In particular, in the case where the salt rejection of the RO membrane before the rejection improving treatment is 95% or less, especially 90% or less, the method according to the present invention is applied favorably.

[0073]

The form of the RO membrane module is not specifically limited. Examples can include a tubular membrane module, a flat sheet membrane module, a spiral wound membrane module, and a hollow fiber membrane module.

[0074]

[Water treatment method]

A water treatment method according to the present invention uses an RO membrane subjected to a rejection

improving treatment by the rejection improver or the rejection improving method according to the present invention and is effectively applied to water treatments for recovery·reuse of high-concentration or low-concentration TOC-containing effluent discharged in an electronic device manufacturing field, a semiconductor manufacturing field, and other various industrial fields, production of ultrapure water from industrial water and city water, or water treatment in other fields.

The water to be treated, which is treated by the RO membrane apparatus according to the present invention, is not specifically limited. However, electrolyte-containing water is suitable. For example, organic matter-containing water having an electrical conductivity of 2 to 10,000 mS/m, and preferably about 10 to 7,000 mS/m is suitable. Examples of such organic matter-containing water can include electronic device manufacturing plant effluent, transportation machine manufacturing plant effluent, organic synthesis plant effluent, printing and plate-making·painting plant effluent, and primary treatment water thereof, although not limited to them.

EXAMPLES

[0075]

The present invention will be described below more specifically with reference to comparative examples and examples.

[0076]

In the following, a flat sheet membrane tester shown in Fig. 3 was used as a performance evaluation apparatus.

In this flat sheet membrane tester, a flat sheet membrane cell 2 is disposed at an intermediate position in the height direction of a cylindrical container 1 with a bottom and a lid, so as to partition the inside of the container into a raw water chamber 1A and a permeate water chamber 1B, this container 1 is disposed on a stirrer 3, water to be treated is fed to the raw water chamber 1A with a pump 4 through a pipe 11 while the inside of the raw water chamber 1A is agitated by rotating a stirring bar 5 in the container 1, permeate water is taken out of the permeate water chamber 1B through a pipe 12 and, in addition, concentrated water is taken out of the raw water chamber 1A through a pipe 13. The pipe 13 to take out the concentrated water is provided with a manometer 6 and a pressure valve 7.

[0077]

In this regard, the RO permeate flux, the salt rejection (NaCl rejection), and the IPA rejection of a evaluated membrane were calculated on the basis of the following formulae, respectively.

permeate flux [$\text{m}^3/(\text{m}^2\text{d})$] = amount of permeate water [m^3/d]/membrane area [m^2] $\times$ temperature conversion factor [-]

salt rejection [%] = $(1 - \text{electrical conductivity of permeate water } [\text{mS/m}] / \text{electrical conductivity of concentrated water } [\text{mS/m}]) \times 100$

IPA rejection [%] = $(1 - \text{TOC of permeate water})$

$[\text{mg/L}]/\text{TOC of concentrated water} [\text{mg/L}] \times 100$

[0078]

[Rejection improving test I]

The following degraded membrane was used as the membrane of the flat sheet membrane cell 2 of the flat sheet tester, and the test was performed, where the rejection improver, the water to be treated for performance evaluation, and the performance evaluation condition were as described below.

Degraded membrane: a membrane prepared by immersing Ultra-low pressure reverse osmosis membrane ES20 produced by NITTO DENKO CORPORATION in an aqueous solution containing 1 percent by weight of hydrogen peroxide and 1 mg/L of ferric chloride in terms of iron content for 24 hours to induce accelerated degradation. The permeate flux, the salt rejection, and the IPA rejection of this degraded membrane were $1.1 \text{ m}^3/(\text{m}^2 \cdot \text{d})$, 90%, and 72%, respectively. The permeate flux, the salt rejection, and the IPA rejection of an original membrane (fresh, not degraded ES20 membrane) were $0.8 \text{ m}^3/(\text{m}^2 \cdot \text{d})$, 98%, and 88%, respectively.

Constituents of rejection improver: arginine (produced by Ajinomoto Healthy Supply Co., Inc., molecular weight 174), aspartame (produced by Ajinomoto Healthy Supply Co., Inc., molecular weight 294), and tannic acid AL (hereafter referred to as tannic acid, produced by Fuji Chemical Industry Co., Ltd., molecular weight 500 or more), all of them are food additive

Water to be treated for performance evaluation: water in which 500 mg/L of NaCl and 100 mg/L of IPA were dissolved in ultrapure water

Performance evaluation condition: operation pressure 0.75 MPa, temperature $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$

[0079]

<Comparative example 1>

Powders of three components constituting the rejection improver were directly dissolved into pure water in such a way that each of them became 10 g/L. As a result, insoluble aggregates were generated and it was not possible to use for a rejection improving treatment.

[0080]

<Example 1>

Powders of arginine and aspartame were mixed on an "as-is" basis at a weight ratio of 1:1 and were dissolved into pure water separately from tannic acid in such a way that each component became 10 g/L. Aspartame was dissolved easily because arginine was present together. The pH of the aqueous solution containing aspartame and arginine was 9.0, and the pH of the aqueous solution containing tannic acid was 3.7.

Thereafter, these two aqueous solutions were dropped to pure water so as to be diluted and mixed in such a way that the concentration of each component became 50 mg/L and, thereby, a clear aqueous solution was obtained.

The resulting mixed aqueous solution was passed through

the degraded membrane for 5 hours to perform a rejection improving treatment. As a result, the permeate flux, the salt rejection, and the IPA rejection of the RO membrane after the treatment were recovered to $0.8 \text{ m}^3/(\text{m}^2 \cdot \text{d})$, 98.5%, and 87%, respectively.

[0081]

[Rejection improving test II]

The following degraded membrane was used as the membrane of the flat sheet membrane cell 2 of the flat sheet tester, and the test was performed, where the rejection improver, the water to be treated for performance evaluation, and the performance evaluation condition were as described below.

Degraded membrane: a membrane prepared by immersing Ultra-low pressure reverse osmosis membrane ES20 produced by NITTO DENKO CORPORATION in an aqueous solution containing 1 percent by weight of hydrogen peroxide and 1 mg/L of ferric chloride in terms of iron content for 24 hours to induce accelerated degradation. The permeate flux, the salt rejection, and the IPA rejection of this degraded membrane were $0.95 \text{ m}^3/(\text{m}^2 \cdot \text{d})$, 95%, and 81%, respectively. The permeate flux, the salt rejection, and the IPA rejection of an original membrane (fresh, not degraded ES20 membrane) were as described above.

Constituents of rejection improver: glycine (produced by Wako Pure Chemical Industries, Ltd., molecular weight 75), arginine (produced by Ajinomoto Healthy Supply Co., Inc.,

molecular weight 174), and tannic acid AL (hereafter referred to as tannic acid, produced by Fuji Chemical Industry Co., Ltd., molecular weight 500 or more)

Water to be treated for performance evaluation: water in which 500 mg/L of NaCl and 100 mg/L of IPA were dissolved in ultrapure water

Performance evaluation condition: operation pressure 0.75 MPa, temperature $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$

[0082]

<Comparative example 2>

Glycine, arginine, and tannic acid were dissolved into pure water individually in such a way that each of them became 30 g/L. They were mixed in such a way that the concentration of each of them became 10 g/L. As a result, aggregates were generated immediately after mixing, and it was not possible to use for a rejection improving treatment.

[0083]

<Comparative example 3>

Glycine, arginine, and tannic acid were dissolved individually in such a way that each of them became 30 g/L. Each of them was stored at -5°C for a month and, thereby, each of them froze. They were returned to ambient temperature and were melted. As a result, precipitates were generated in the tannic acid aqueous solution, and it was not possible to use for a rejection improving treatment.

[0084]

<Comparative example 4>

Equal amounts of glycine, arginine, and tannic acid in the powder state were mixed. The resulting mixed powder was stored at -5°C for a month and no change was observed in the state of the powder. The resulting mixed powder was dissolved into pure water in such a way that the concentration of each of them became 10 g/L. As a result, aggregates were generated, and it was not possible to use for a rejection improving treatment.

[0085]

<Example 2>

Glycine and arginine were mixed at a weight ratio of 1:1 in the powder state and tannic acid was in the powder state alone. Each powdered chemical agent was stored at a temperature of -5°C for a month. Thereafter, the two powdered chemical agents were dissolved into pure water individually in such a way that the concentration of each component became 10 g/L. The pH of the aqueous solution containing glycine and arginine was 9.6, and the pH of the tannic acid aqueous solution was 3.7. These glycine·arginine aqueous solution and the tannic acid aqueous solution were used, and the rejection improving treatment of the degraded membrane was performed in the method described below.

That is, the glycine·arginine aqueous solution and the tannic acid aqueous solution were line-injected individually into the flow path of the water to be treated, while adjustment was performed in such a way that the flow rate of

each aqueous solution became 1/5,000 of the flow rate of the water to be treated, i.e. the concentration of each component after joining to the water to be treated became 2 mg/L. After injection was started, the performance of the degraded membrane was changed, and after 72 hours had elapsed, the permeate flux, the salt rejection, and the IPA rejection became $0.8 \text{ m}^3/(\text{m}^2 \cdot \text{d})$, 98.7%, and 89%, respectively. [0086]

[Discussion]

The following are clear from the above-described results.

i) Arginine and aspartame are mixed to form a powdered chemical agent. Meanwhile, tannic acid is used as a powdered chemical agent on an "as-is" basis. Each of them is made into a high-concentration aqueous solution. Thereafter, the aqueous solutions are diluted and mixed and, thereby, it is possible to use for the rejection improving treatment of the RO membrane effectively without generating aggregates.

ii) Glycine and arginine are mixed to form a powdered chemical agent. Meanwhile, tannic acid is used as a powdered chemical agent on an "as-is" basis, and they are stored separately. Thereafter, when the agents are dissolved into water, homogeneous and stable aqueous solutions can be prepared without generating aggregates. The aqueous solutions are diluted and mixed by line injection, and it is possible to use for the rejection

improving treatment of the RO membrane effectively without generating aggregates.

[0087]

The present invention has been explained in detail with reference to specific modes. However, it is understood by those skilled in the art that various modifications can be made within the bound of not departing from the spirit and scope of the present invention.

The present application contains subject matter related to Japanese patent application (Japanese Patent Application No. 2012-088478) filed on April 9, 2012, which is hereby incorporated by reference herein in its entirety.

Reference Signs List

[0088]

- 1 container
- 1A raw water chamber
- 1B permeate water chamber
- 2 flat sheet cell
- 3 stirrer

CLAIMS

1 A rejection improver of a reverse osmosis membrane, characterized by comprising at least two types of organic compounds having different molecular weights, wherein the rejection improver of a reverse osmosis membrane contains at least an organic compound, which has a molecular weight of 60 or more and less than 500 and which has an amino group, and tannic acid, and the organic compound having an amino group and the tannic acid are stored as two powdered chemical agents different from each other.

2 The rejection improver of a reverse osmosis membrane, according to Claim 1, characterized in that when the two powdered chemical agents are made into their respective aqueous solutions having each organic compound concentration of 1 to 200 g/L, the pH of an aqueous solution of one powdered chemical agent containing the organic compound having an amino group is 7 or more, and the pH of an aqueous solution of the other powdered chemical agent containing the tannic acid is less than 7.

3 The rejection improver of a reverse osmosis membrane, according to Claim 1, characterized in that the organic compound, which has a molecular weight of 60 or more and less than 500 and which has an amino group, contains a first amino compound having a molecular weight of less than 200

and a second amino group having a molecular weight of 200 or more and less than 500.

4 The rejection improver of a reverse osmosis membrane, according to Claim 1, characterized in that the first amino compound is a basic amino acid and the second amino compound is peptide or a derivative thereof.

5 A method for improving the rejection of a reverse osmosis membrane by treating the reverse osmosis membrane through the use of an aqueous solution of the rejection improver according to any one of Claims 1 to 4, the method characterized by comprising the steps of preparing an aqueous solution having an organic compound concentration (in the case where the powdered chemical agent contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of 1 to 200 g/L by dissolving at least one powdered chemical agent of the two powdered chemical agents into water and diluting the aqueous solution in such a way that the organic compound concentration (in the case where the powdered chemical agent contains at least two types of organic compounds, this organic compound concentration refers to each organic compound concentration) of the aqueous solution becomes 0.1 to 1000 mg/L.

6 A method for improving the rejection of a reverse

osmosis membrane by treating the reverse osmosis membrane through the use of an aqueous solution of the rejection improver according to any one of Claims 1 to 4, the method characterized by comprising the step of preparing an aqueous solution having each organic compound concentration of 1 to 1000 mg/L by dissolving the two powdered chemical agents into water independently and mixing the resulting aqueous solutions.

7 A method for improving the rejection of a reverse osmosis membrane by treating the reverse osmosis membrane through the use of an aqueous solution of the rejection improver according to any one of Claims 1 to 4, the method characterized by comprising the step of diluting and mixing aqueous solutions, which are obtained by dissolving the two powdered chemical agents into water independently, by line-injecting them from mutually independent positions.

8 A reverse osmosis membrane subjected to a rejection improving treatment through the use of the rejection improver according to any one of Claims 1 to 4.

9 A reverse osmosis membrane subjected to a rejection improving treatment by the method for improving the rejection according to Claim 5.

10 A reverse osmosis membrane subjected to a rejection

improving treatment by the method for improving the rejection according to Claim 6.

11 A reverse osmosis membrane subjected to a rejection improving treatment by the method for improving the rejection according to Claim 7.

12 A reverse osmosis membrane subjected to a rejection improving treatment by the method for improving the rejection according to Claim 8.