

DESCRIPTION

WATER TREATMENT METHOD USING REVERSE-OSMOSIS MEMBRANE

5 TECHNICAL FIELD

[0001]

The present invention relates to a water treatment method using a reverse osmosis membrane (RO membrane).

10 BACKGROUND

[0002]

In water treatment methods that use a reverse osmosis membrane (RO membrane), the use of various antimicrobial agents (slime inhibitors) as biofouling countermeasures is typical. Chlorine-based oxidizing agents such as hypochlorous acid and the like are
15 representative antimicrobial agents, and are typically added to a stage prior to the reverse osmosis membrane for the purpose of sterilizing the system. Because chlorine-based oxidizing agents are highly likely to degrade the reverse osmosis membrane, the chlorine-based oxidizing agent is generally either reductively decomposed immediately prior to the reverse osmosis membrane, or only introduced into the reverse osmosis
20 membrane intermittently.

[0003]

Further, a method for introducing a combined chlorine agent composed of a chlorine-based oxidizing agent and a sulfamic acid compound as an antimicrobial agent (slime inhibitor) into the water to be treated by a reverse osmosis membrane (see Patent
25 Document 1), and a method for adding a mixture or a reaction product of a bromine-based oxidizing agent, or a reaction product of a bromine-based compound and a chlorine-based oxidizing agent, and a sulfamic acid compound to the water to be treated (see Patent Document 2) are already known.

[0004]

Antimicrobial agents containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound are very effective as they not only exhibit a superior sterilizing function, but are also unlikely to cause oxidative deterioration of polyamide-based reverse osmosis membranes, have a high rejection rate by reverse osmosis membranes, and have little effect on the quality of the latter-stage treated water (permeate).

CITATION LIST

10 PATENT LITERATURE

[0005]

Patent Document 1: JP 2006-263510 A

Patent Document 2: JP 2015-062889 A

15 SUMMARY

TECHNICAL PROBLEM

[0006]

However, because the majority of the antimicrobial agent is rejected by the reverse osmosis membrane, even if the antimicrobial agent is effective on the primary side of the reverse osmosis membrane, the permeate line on the secondary side may sometimes still suffer from slime contamination. Particularly in those cases where the water to be treated contains organic matter having a low molecular weight (for example, a molecular weight of 200 or less), because the rejection rate for this low-molecular weight organic matter by the reverse osmosis membrane is low, even if the antimicrobial agent is effective on the primary side of the reverse osmosis membrane, slime contamination caused by the low-molecular weight organic matter may sometimes still occur on the secondary side.

[0007]

An object of the present invention is to provide a water treatment method using a reverse osmosis membrane, wherein the method suppresses slime contamination even on the secondary side of the reverse osmosis membrane, and suppressing oxidative deterioration of the reverse osmosis membrane.

5

SOLUTION TO PROBLEM

[0008]

The present invention provides a water treatment method using a reverse osmosis membrane, in which a water to be treated is treated using the reverse osmosis membrane, wherein an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound is introduced into the water to be treated, which contains ammonia.

10

[0009]

Further, the present invention also provides a water treatment method using a reverse osmosis membrane, in which a water to be treated is treated using the reverse osmosis membrane, wherein an antimicrobial agent containing bromine and a sulfamic acid compound is introduced into the water to be treated, which contains ammonia.

15

[0010]

In the water treatment method using a reverse osmosis membrane described above, the concentration of the antimicrobial agent or the concentration of the ammonia is preferably adjusted so that the ratio of the concentration of the ammonia relative to the total chlorine concentration in the water to be treated falls within a range from 0.01 to 1.

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[0011]

In the water treatment method using a reverse osmosis membrane described above, the reverse osmosis membrane is preferably an anionically charged membrane.

25

[0012]

<Water Treatment Method using Reverse Osmosis Membrane>

The water treatment method using a reverse osmosis membrane according to an embodiment of the present invention is a method for introducing an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound into a water to be treated that contains ammonia. The "antimicrobial agent containing a bromine-based oxidizing agent and a sulfamic acid compound" may be an antimicrobial agent containing a stabilized hypobromous acid composition containing a mixture of a "bromine-based oxidizing agent" and a "sulfamic acid compound", or may be an antimicrobial agent containing a stabilized hypobromous acid composition containing a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound". The "antimicrobial agent containing a chlorine-based oxidizing agent and a sulfamic acid compound" may be an antimicrobial agent containing a stabilized hypochlorous acid composition containing a mixture of a "chlorine-based oxidizing agent" and a "sulfamic acid compound", or may be an antimicrobial agent containing a stabilized hypochlorous acid composition containing a "reaction product of a chlorine-based oxidizing agent and a sulfamic acid compound".

[0018]

In other words, the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention is a method for treating a water to be treated with a reverse osmosis membrane, wherein a mixture of a "bromine-based oxidizing agent" and a "sulfamic acid compound", or a mixture of a "chlorine-based oxidizing agent" and a "sulfamic acid compound" is introduced into a water to be treated that contains ammonia. As a result, it is thought that a stabilized hypobromous acid composition or a stabilized hypochlorous acid composition is produced within the water being treated.

[0019]

Further, the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention is a method for treating a water to be treated with a

reverse osmosis membrane, wherein a stabilized hypobromous acid composition that is a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" or a stabilized hypochlorous acid composition that is a "reaction product of a chlorine-based oxidizing agent and a sulfamic acid compound" is introduced into a water to be treated that
5 contains ammonia.

[0020]

Specifically, the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention is a method for treating a water to be treated with a reverse osmosis membrane, wherein a mixture of "bromine", "bromine
10 chloride", "hypobromous acid" or a "reaction product of sodium bromide and hypochlorous acid", and a "sulfamic acid compound" is introduced into a water to be treated that contains ammonia. Alternatively, a mixture of "hypochlorous acid" and a "sulfamic acid compound" may be introduced into the water to be treated that contains ammonia.

[0021]

15 Further, the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention is a method for treating a water to be treated with a reverse osmosis membrane, wherein, for example, a stabilized hypobromous acid composition that is a "reaction product of bromine and a sulfamic acid compound", "a reaction product of bromine chloride and a sulfamic acid compound", a "reaction product
20 of hypobromous acid and a sulfamic acid compound" or a "reaction product of a sulfamic acid compound with a reaction product of sodium bromide and hypochlorous acid" is introduced into a water to be treated that contains ammonia. Alternatively, a stabilized hypochlorous acid composition that is a "reaction product of hypochlorous acid and a sulfamic acid compound" may be introduced into the water to be treated that contains
25 ammonia.

[0022]

As a result of intensive investigation, the inventors of the present invention discovered that when a water to be treated contains ammonia, an antimicrobial agent

containing a stabilized hypobromous acid composition or a stabilized hypochlorous acid permeates more readily through a reverse osmosis membrane. By utilizing this phenomenon, and introducing an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound into a water to be treated that contains ammonia, a water treatment method for treating a water to be treated using a reverse osmosis membrane can be provided in which slime contamination can be suppressed even on the secondary side of the reverse osmosis membrane, and oxidative deterioration of the reverse osmosis membrane can be suppressed.

[0023]

10 In this manner, in the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, the stabilized hypobromous acid composition or stabilized hypochlorous acid composition exhibits a similar or superior slime suppression effect to chlorine-based oxidizing agents such as hypochlorous acid, and yet has a smaller degradation effect on the reverse osmosis membrane compared with
15 chlorine-based oxidizing agents, and therefore oxidative deterioration of the reverse osmosis membrane can be suppressed, while suppressing fouling of the reverse osmosis membrane. As a result, the stabilized hypobromous acid composition or stabilized hypochlorous acid composition used in the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention functions favorably as a
20 slime inhibitor for use in a water treatment method for treating a water to be treated using a reverse osmosis membrane.

[0024]

Among the water treatment methods using a reverse osmosis membrane according to embodiments of the present invention, in the case of an "antimicrobial agent containing a
25 bromine-based oxidizing agent and a sulfamic acid compound", because a chlorine-based oxidizing agent does not exist, the degradative effect on the reverse osmosis membrane is particularly minor. When a chlorine-based oxidizing agent exists, the production of chloric acid can be a concern.

[0025]

Among the water treatment methods using a reverse osmosis membrane according to embodiments of the present invention, when the "bromine-based oxidizing agent" is bromine, because a chlorine-based oxidizing agent does not exist, the degradative effect on the reverse osmosis membrane is remarkably low.

[0026]

In the water treatment methods using a reverse osmosis membrane according to embodiments of the present invention, the "bromine-based oxidizing agent" or "chlorine-based oxidizing agent" and the "sulfamic acid compound" may, for example, be injected into the water to be treated that contains ammonia using a chemical feed pump or the like. The "bromine-based oxidizing agent" or "chlorine-based oxidizing agent" and the "sulfamic acid compound" may be added separately to the water to be treated, or the neat liquids may be mixed together and then added to the water to be treated.

[0027]

Further, the "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" or the "reaction product of a chlorine-based oxidizing agent and a sulfamic acid compound" may, for example, be injected into the water to be treated that contains ammonia using a chemical feed pump or the like.

[0028]

In the water treatment methods using a reverse osmosis membrane according to embodiments of the present invention, the ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of the "bromine-based oxidizing agent" or the "chlorine-based oxidizing agent" is preferably 1 or greater, and is more preferably within a range from at least 1 to not more than 2. If the ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of the "bromine-based oxidizing agent" or the "chlorine-based oxidizing agent" is less than 1, then there is a possibility that deterioration of the membrane may occur, whereas if the ratio exceeds 2, then the production costs may sometimes increase.

[0029]

The total chlorine concentration contacting the reverse osmosis membrane, calculated as an effective equivalent chlorine concentration, is preferably from 0.01 to 100 mg/L. If this concentration is less than 0.01 mg/L, then a satisfactory slime suppression
5 effect may not be obtainable, whereas if the concentration is greater than 100 mg/L, then there is a possibility that deterioration of the reverse osmosis membrane or corrosion of the piping or the like may occur.

[0030]

The antimicrobial agent is preferably introduced so that the ratio of the concentration
10 of ammonia relative to the total chlorine concentration in the water to be treated (ammonia concentration (mg/L)/ antimicrobial agent concentration (total chlorine concentration: mg/L)) falls within a range from 0.01 to 1, and more preferably falls within a range from 0.01 to 0.5. Introducing the antimicrobial agent so that the ratio of the ammonia concentration relative to the total chlorine concentration is at least 0.01 ensures a
15 satisfactory improvement in the permeation rate of the antimicrobial agent, and is consequently preferred. If the ratio of the ammonia concentration relative to the total chlorine concentration in the water to be treated is less than 0.01, then the improvement in the permeation rate of the antimicrobial agent may not be adequate, whereas if the ratio exceeds 1, then the effect of the ammonia addition in improving the permeation rate of the
20 antimicrobial agent may not manifest satisfactorily.

[0031]

In those cases where the water to be treated does not contain ammonia, an ammonia salt may be added, or the water to be treated may be mixed with another ammonia-containing water.

25 [0032]

In those cases where the water to be treated contains organic matter that permeates through the reverse osmosis membrane in a concentration of at least 0.5 mg/L, and particularly a concentration of at least 1.0 mg/L but not more than 500 mg/L, the water

treatment method using a reverse osmosis membrane according to an embodiment of the present invention can be applied particularly favorably. If the amount of organic matter that permeates through the reverse osmosis membrane is less than 0.5 mg/L in the water to be treated, then slime contamination of the secondary side of the reverse osmosis

5 membrane is unlikely to occur.

[0033]

In this description, low-molecular weight organic matter describes organic matter having a molecular weight of 200 or less, and examples include various compounds having a molecular weight of 200 or less, including alcohol compounds such as methanol, ethanol
10 and isopropyl alcohol, amine compounds such as monoethanolamine and urea, and tetraalkylammonium salts such as tetramethylammonium hydroxide.

[0034]

Examples of the bromine-based oxidizing agent include bromine (liquid bromine), bromine chloride, bromic acid, bromate salts, and hypobromous acid and the like. The
15 hypobromous acid may be produced by reacting a bromide such as sodium bromide with a chlorine-based oxidizing agent such as hypochlorous acid.

[0035]

Among these, compared with the formulation of "hypochlorous acid, a bromine compound and sulfamic acid" and the formulation of "bromine chloride and sulfamic acid"
20 and the like, formulations that use bromine such as "bromine and a sulfamic acid compound (a mixture of bromine and a sulfamic acid compound)" or a "reaction product of bromine and a sulfamic acid compound" tend to exhibit lower production of the by-product bromic acid, and are less likely to cause degradation of the reverse osmosis membrane, and are consequently preferred as slime inhibitors for reverse osmosis membranes.

25 [0036]

In other words, the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention preferably involves introducing bromine and a sulfamic acid compound (or introducing a mixture of bromine and a

sulfamic acid compound) into a water to be treated that contains ammonia. Further, introducing a reaction product of bromine and a sulfamic acid compound into the water to be treated is also preferred.

[0037]

- 5 Examples of the bromine compound include sodium bromide, potassium bromide, lithium bromide, ammonium bromide and hydrobromic acid. Among these, in terms of production costs and the like, sodium bromide is preferred.

[0038]

- 10 Examples of the chlorine-based oxidizing agent include chlorine gas, chlorine dioxide, hypochlorous acid or salts thereof, chlorous acid or salts thereof, chloric acid or salts thereof, perchloric acid or salts thereof, and chlorinated isocyanuric acid or salts thereof. Among these, examples of the salts include alkali metal salts of hypochlorous acid such as sodium hypochlorite and potassium hypochlorite, alkaline earth metal salts of hypochlorous acid such as calcium hypochlorite and barium hypochlorite, alkali metal salts of chlorous acid such as sodium chlorite and potassium chlorite, alkaline earth metal salts of chlorous acid such as barium chlorite, other metal salts of chlorous acid such as nickel chlorite, alkali metal salts of chloric acid such as ammonium chlorate, sodium chlorate and potassium chlorate, and alkaline earth metal salts of chloric acid such as calcium chlorate and barium chlorate. Any one of these chlorine-based oxidizing agents may be used
- 15 alone, or a combination of two or more oxidizing agents may be used. In terms of ease of handling and the like, the use of sodium hypochlorite as the chlorine-based oxidizing agent is preferred.

[0039]

- 25 The sulfamic acid compound is a compound represented by general formula (1) shown below.



(In the formula, each R independently represents a hydrogen atom or an alkyl group having a carbon number of 1 to 8.)

[0040]

Examples of the sulfamic acid compound, in addition to sulfamic acid (amidosulfuric acid) in which the two R groups are both hydrogen atoms, include sulfamic acid compounds in which one of the two R groups is a hydrogen atom and the other is an

5 alkyl group having a carbon number of 1 to 8, such as N-methylsulfamic acid, N-ethylsulfamic acid, N-propylsulfamic acid, N-isopropylsulfamic acid and N-butylsulfamic acid, sulfamic acid compounds in which the two R groups are both alkyl groups having a carbon number of 1 to 8, such as N,N-dimethylsulfamic acid, N,N-diethylsulfamic acid, N,N-dipropylsulfamic acid, N,N-dibutylsulfamic acid,

10 N-methyl-N-ethylsulfamic acid and N-methyl-N-propylsulfamic acid, and sulfamic acid compounds in which one of the two R groups is a hydrogen atom and the other is an aryl group having a carbon number of 6 to 10, such as N-phenylsulfamic acid, as well as salts of the above acids. Examples of the sulfamic acid salts include alkali metal salts such as sodium salts and potassium salts, alkaline earth metal salts such as calcium salts, strontium

15 salts and barium salts, other metal salts such as manganese salts, copper salts, zinc salts, iron salts, cobalt salts and nickel salts, as well as ammonium salts and guanidine salts. One of these sulfamic acid compounds or salts may be used alone, or a combination of two or more compounds or salts may be used. In terms of the environmental burden and the like, the use of sulfamic acid (amidosulfuric acid) as the sulfamic acid compound is

20 preferred.

[0041]

In the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, an alkali is preferably also introduced. Examples of the alkali include alkali hydroxides such as sodium hydroxide and potassium hydroxide.

25 In terms of achieving good product stability and the like at low temperatures, a combination of sodium hydroxide and potassium hydroxide may also be used. Further, the alkali may also be used not as a solid, but in the form of an aqueous solution.

[0042]

The water treatment method using a reverse osmosis membrane according to an embodiment of the present invention can be applied favorably to polyamide-based polymer membranes, which are currently the most widely used reverse osmosis membranes.

Polyamide-based polymer membranes have comparatively low resistance to oxidizing

5 agents, and if free chlorine or the like is kept in continuous contact with a polyamide-based polymer membrane, then a marked deterioration in membrane performance may occur.

However, in the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, this type of marked deterioration in membrane performance is almost non-existent, even for polyamide polymer membranes.

10 [0043]

Reverse osmosis membranes include neutral membranes, anionically charged membranes and cationically charged membranes. In this description, a neutral membrane indicates a membrane for which the zeta potential at pH 7.0, measured using the zeta potential measurement method described in the following examples, is within a range from
15 -5 to 5 (mV), whereas an anionically charged membrane indicates a membrane for which the zeta potential at pH 7.0 is less than -5 (mV).

[0044]

Examples of commercially available neutral membranes include BW30XFR (manufactured by The Dow Chemical Company), LFC3 (manufactured by Nitto Denko
20 Corporation), and TML20 (manufactured by Toray Industries, Inc.).

[0045]

Examples of commercially available anionically charged membranes include OFR-265 (manufactured by Organo Corporation), ES15, ES20, CPA3 and CPA5 (all manufactured by Nitto Denko Corporation), and RE-8040BLN (manufactured by
25 Woongjin Chemical Co., Ltd.).

[0046]

In the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, compared with using a neutral membrane, using an

anionically charged membrane yields a higher permeation rate for the antimicrobial agent, and can enable better suppression of slime contamination on the secondary side of the reverse osmosis membrane.

[0047]

5 In the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, when the permeate is not used at the use point, the obtained RO permeate may be recirculated to the primary side of the reverse osmosis membrane together with the RO concentrate, and an antimicrobial agent is preferably added to and introduced into the water to be treated only when the permeate is not used at
10 the use point. As a result, an effect can be achieved wherein sterilization of the RO permeate line is performed, but the antimicrobial agent may be absent from the permeate when the permeate is used.

[0048]

 In the water treatment method using a reverse osmosis membrane according to an
15 embodiment of the present invention, the water to be treated that is supplied to the reverse osmosis membrane device containing the reverse osmosis membrane has a pH that is preferably at least 5.5, more preferably at least 6.0, and even more preferably 6.5 or higher. If the pH of the water to be treated is less than 5.5, then the volume of permeate may sometimes decrease. Further, in terms of the upper limit for the pH of the water to be
20 treated, there are no particular limitations, provided the pH does not exceed the typical upper limit pH for a reverse osmosis membrane (for example, pH 10), but if consideration is given to scale precipitation of hard components such as calcium, then operating the device, for example, at a pH of 9.0 or lower is preferred. When using the water treatment method using a reverse osmosis membrane according to an embodiment of the present
25 invention, by performing operations with the pH of the water to be treated at 5.5 or higher, degradation of the reverse osmosis membrane and deterioration in the water quality of the treated water (the permeate) can be suppressed, and a satisfactory volume of permeate can be ensured, while achieving an adequate slime suppression effect.

[0049]

In those cases where scale develops in the reverse osmosis membrane device when the pH of the water to be treated is 5.5 or higher, a dispersant may be used in combination with the antimicrobial agent described above for the purpose of scale suppression.

- 5 Examples of the dispersant include polyacrylic acid, polymaleic acid and phosphonic acid. The amount of the dispersant added to the water to be treated, for example, may be within a range from 0.1 to 1,000 mg/L in terms of the concentration within the RO concentrate.

[0050]

- Further, one method for suppressing the occurrence of scale without using a
10 dispersant involves adjusting the operating conditions for the reverse osmosis membrane device such as the recovery rate so that the silica concentration in the RO concentrate is no higher than the degree of solubility, and the Langelier index, which is an indicator for calcium scale, is not more than 0.

[0051]

- 15 Examples of applications for the reverse osmosis membrane device include pure water production, seawater desalination and wastewater recovery.

[0052]

<Antimicrobial Agent>

- The antimicrobial agent according to an embodiment of the present invention
20 contains a stabilized hypobromous acid composition or stabilized hypochlorous acid composition containing a mixture of a "bromine-based oxidizing agent or a chlorine-based oxidizing agent" and a "sulfamic acid compound", and may also contain an alkali.

[0053]

- Further, the antimicrobial agent according to an embodiment of the present invention
25 contains a stabilized hypobromous acid composition containing a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound", or a stabilized hypochlorous acid composition containing a "reaction product of a chlorine-based oxidizing agent and a sulfamic acid compound", and may also contain an alkali.

[0054]

The bromine-based oxidizing agent, the bromine compound, the chlorine-based oxidizing agent, and the sulfamic acid compound are as described above.

[0055]

5 In order to achieve less degradation of the reverse osmosis membrane, the antimicrobial agent according to an embodiment of the present invention preferably either contains bromine and a sulfamic acid compound (a mixture of bromine and a sulfamic acid compound), for example, a mixture of bromine, a sulfamic acid compound, an alkali and water, or alternatively, contains a reaction product of bromine and a sulfamic acid
10 compound, for example, a mixture of a reaction product of bromine and a sulfamic acid compound, an alkali and water.

[0056]

 Compared with antimicrobial agents containing a chlorine-based oxidizing agent and a sulfamic acid compound (such as chlorosulfamic acid), of the various antimicrobial
15 agents according to embodiments of the present invention, antimicrobial agents containing a bromine-based oxidizing agent and a sulfamic acid compound, and particularly antimicrobial agents containing bromine and a sulfamic acid compound, exhibit higher oxidizing power, and markedly higher slime suppression and slime-detaching power, and yet cause almost none of the marked membrane degradation observed for other
20 compositions of similarly high oxidizing power such as hypochlorous acid. At typical usage concentrations, the effects on membrane degradation can be essentially ignored. As a result, these agents are ideal as antimicrobial agents.

[0057]

 Unlike hypochlorous acid, the antimicrobial agents according to embodiments of the
25 present invention undergo almost no permeation through the reverse osmosis membrane, and therefore have almost no effect on the treated water quality. Further, because the concentration can be measured on site in a similar manner to hypochlorous acid or the like, more accurate concentration control is possible.

[0058]

The pH of the antimicrobial agent is, for example, higher than 13.0, and is preferably higher than 13.2. If the pH of the antimicrobial agent is 13.0 or lower, then the effective halogen in the antimicrobial agent may sometimes become unstable.

5 [0059]

The bromate concentration in the antimicrobial agent is preferably less than 5 mg/kg. If the bromate concentration in the antimicrobial agent is 5 mg/kg or greater, then the concentration of bromate ions in the RO permeate may increase.

[0060]

10 <Method for Producing Antimicrobial Agent>

The antimicrobial agent according to an embodiment of the present invention is obtained by mixing a bromine-based oxidizing agent or a chlorine-based oxidizing agent with a sulfamic acid compound, and an alkali may also be mixed into the agent.

[0061]

15 The method for producing an antimicrobial agent that contains a stabilized hypobromous acid composition containing bromine and a sulfamic acid compound preferably includes a step of adding and reacting bromine, under an inert gas atmosphere, with a mixed solution containing water, an alkali and a sulfamic acid compound, or a step of adding bromine, under an inert gas atmosphere, to a mixed solution containing water, an
20 alkali and a sulfamic acid compound. By performing the addition and inducing the reaction under an inert gas atmosphere, or by performing the addition under an inert gas atmosphere, the bromate ion concentration in the antimicrobial agent can be reduced, and the bromate ion concentration in the RO permeate can be reduced.

[0062]

25 Although there are no particular limitations on the inert gas used, at least one of nitrogen and argon is preferred from a production perspective and the like, and nitrogen is particularly preferred in terms of production costs and the like.

[0063]

The oxygen concentration inside the reaction vessel during the bromine addition is preferably not more than 6%, more preferably not more than 4%, even more preferably not more than 2%, and particularly preferably 1% or less. If the oxygen concentration inside the reaction vessel during the bromine reaction exceeds 6%, then the amount of bromic acid produced in the reaction system may sometimes increase.

[0064]

The proportion of bromine added is preferably not more than 25 wt% relative to the total weight of the antimicrobial agent, and is more preferably at least 1 wt% but not more than 20 wt%. If the proportion of bromine added exceeds 25 wt% relative to the total weight of the antimicrobial agent, then the amount of bromic acid produced in the reaction system may sometimes increase. If the proportion is less than 1 wt%, then the sterilizing effect may be inferior.

[0065]

The reaction temperature during the bromine addition is preferably controlled within a range from at least 0°C to not more than 25°C, and in terms of production costs and the like, is more preferably controlled within a range from at least 0°C to not more than 15°C. If the reaction temperature during the bromine addition exceeds 25°C, then the amount of bromic acid produced in the reaction system may sometimes increase, whereas if the temperature is less than 0°C, then the reaction system may freeze.

20

EXAMPLES

[0066]

The present invention is described below in further detail using examples and a comparative example, but the present invention is in no way limited by the following examples.

[0067]

[Preparation of Stabilized Hypobromous Acid Composition (Composition 1)]

Liquid bromine: 16.9 wt%, sulfamic acid: 10.7 wt%, sodium hydroxide: 12.9 wt%, potassium hydroxide: 3.94 wt% and water: the balance were mixed together under a nitrogen atmosphere to prepare a stabilized hypobromous acid composition (composition 1). The pH of the stabilized hypobromous acid composition was 14, and the total chlorine concentration was 7.5 wt%. A detailed description of the method for preparing the stabilized hypobromous acid composition is presented below.

[0068]

A 2 L four-neck flask into which nitrogen gas was injected continuously at a flow rate controlled by a mass flow controller so that the oxygen concentration inside the reaction vessel was maintained at 1% was charged with 1,436 g of water and 361 g of sodium hydroxide, and following mixing, 300 g of sulfamic acid was added and mixed, and with the flask then cooled to maintain the temperature of the reaction solution at 0 to 15°C, 473 g of liquid bromine was added, and 230 g of a 48% solution of potassium hydroxide was then added, thus obtaining the target stabilized hypobromous acid composition (the composition 1) containing 10.7% of sulfamic acid and 16.9% of bromine relative to the total weight of the composition, and having a ratio for the equivalent weight of sulfamic acid relative to the equivalent weight of bromine of 1.04. Measurement of the pH of the prepared solution using the glass electrode method yielded a value of 14. Measurement of the bromine content of the prepared solution using a method in which the bromine was substituted with iodine using potassium iodide, and a redox titration was then performed using sodium thiosulfate revealed a value of 16.9%, which was 100.0% of the theoretical content (16.9%). Further, the oxygen concentration inside the reaction vessel during the bromine reaction was measured using an "Oxygen Monitor JKO-02 LJDII" manufactured by Jikco Ltd. The bromate concentration was less than 5 mg/kg.

[0069]

The pH measurement was performed under the following conditions.

Electrode type: glass electrode

pH meter: IOL-30 model, manufactured by DKK-TOA Corporation

Electrode calibration: two-point calibration performed using the pH (6.86) of a neutral phosphate standard solution (type 2) manufactured by Kanto Chemical Co., Inc., and the pH (9.18) of a borate standard solution (type 2) manufactured by the same company.

5 Measurement temperature: 25°C

Measured value: the electrode was immersed in the liquid undergoing measurement, the value following stabilization was recorded as the measured value, and the average of three measurements was recorded.

[0070]

10 [Preparation of Stabilized Hypochlorous Acid Composition (Composition 2)]

A 12% aqueous solution of sodium hypochlorite: 50 wt%, sulfamic acid: 12 wt%, sodium hydroxide: 8 wt%, and water: the balance were mixed together to prepare a stabilized hypochlorous acid composition (composition 2). The pH of the composition 2 was 13.7, and the total chlorine concentration was 6.2 wt%.

15 [0071]

[Measurement of Zeta Potential of Reverse Osmosis Membrane]

The zeta potential of the reverse osmosis membrane was measured using a zeta potential and particle size measurement system ELSZ series, manufactured by Otsuka Electronics Co., Ltd. The zeta potential of the reverse osmosis membrane was calculated from the measured electroosmotic plot using the Mori-Okamoto equation and the Smoluchowski equation shown below.

[0072]

(Mori-Okamoto equation)

$$U_{\text{obs}}(z) = AU_0(z/b)^2 + \Delta U_0(z/b) + (1-A)U_0 + U_p$$

25 Here,

z: distance from cell center position

$U_{\text{obs}}(z)$: apparent mobility at z position in cell

A: $1/[(2/3)-(0.420166/K)]$

wherein $K=a/b$: 2a and 2b represent horizontal and vertical lengths of a cell

cross-section, and $a>b$

U_p : true mobility of particle

U_0 : average mobility on upper and lower surfaces of cell

5 ΔU_0 : difference in mobility on upper and lower surfaces of cell

(Smoluchowski equation)

$$\zeta = 4\pi\eta U/\varepsilon$$

Here,

U : electric mobility

10 ε : dielectric constant of solvent

η : viscosity of solvent

[0073]

A 10 mM aqueous solution of NaCl (pH of about 5.4) was used as the measurement solution. For each sample, two sets of pairs each including this aqueous solution and the sample were prepared, one pair was adjusted to an acidic pH (pH 2, 3, 4, 5, 6 or 7) and the other was adjusted to an alkaline pH (pH 8 or 9), and the zeta potential was measured at each pH. The values for pure water at 25°C (refractive index: 1.3328, viscosity: 0.8878, dielectric constant: 78.3) were used for the physical property values of the solvent.

[0074]

20 <Example 1 and Comparative Example 1>

[Test Conditions and Test Method]

The concentration of the antimicrobial agent in the permeate was measured by a flat membrane test. A Membrane Master C70 - F flow-type flat membrane test cell was used for the flat membrane cell. A reverse osmosis membrane manufactured by Nitto Denko Corporation (an anionically charged membrane ES20 (a polyamide-based anionically charged membrane)) was used for the flat membrane. The flat membrane was circular, and had a diameter of 75 mm. The flow is illustrated in FIG.1.

[0075]

For the test water (water to be treated), a solution prepared by adding the antimicrobial agent to ultra-pure water and then using hydrochloric acid or sodium hydroxide to adjust the pH to 7.0 was used. The concentration of the antimicrobial agent was set to a total chlorine concentration of about 6 mg/L. A chiller was used to adjust the water temperature to $25 \pm 1^\circ\text{C}$. The operating pressure for the reverse osmosis membrane was set to 0.75 MPa. The feed water was supplied to the reverse osmosis membrane at 5 L/min. After supplying the water for about 3 hours, the antimicrobial agent concentration (total chlorine concentration) of the water being treated and the permeate were measured. The total chlorine concentration was measured using a multi-item water quality analyzer DR/4000 manufactured by Hach Company, and indicates the value (mg/L, as Cl_2) obtained by measurement using a total chlorine measurement method (the DPD (diethyl-p-phenylenediamine) method).

[0076]

(Example 1)

In Example 1, ammonium chloride was added to the water to be treated to achieve an ammonia concentration of 1 mg/L, the concentration of each antimicrobial agent in the water to be treated and the permeate were measured, and the permeation rate was calculated. The results are shown in Table 1.

[0077]

(Comparative Example 1)

Further, in Comparative Example 1, the concentration of each antimicrobial agent in the water to be treated and the permeate were measured for the case where no ammonium chloride was added to the water to be treated, and the permeation rate was calculated.

The results are shown in Table 2.

[0078]

[Table 1]

Table 1 Example 1 (ammonia concentration: 1 mg/L)

Antimicrobial agent	Antimicrobial agent	Antimicrobial agent	Antimicrobial agent
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	concentration in raw water [mg/L]	concentration in permeate [mg/L]	permeation rate [%]
Stabilized hypobromous acid composition	6.0	1.36	22.7
Chlorosulfamic acid	6.0	0.27	4.5

[0079]

[Table 2]

Table 2 Comparative Example 1 (ammonia concentration: 0 mg/L)

Antimicrobial agent	Antimicrobial agent concentration in raw water [mg/L]	Antimicrobial agent concentration in permeate [mg/L]	Antimicrobial agent permeation rate [%]
Stabilized hypobromous acid composition	6.1	0.03	0.5
Chlorosulfamic acid	5.9	0.11	1.9

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[0080]

In this manner, it is evident that when ammonia exists in the water to be treated, as was the case in Example 1, the antimicrobial agent permeation rate increases.

[0081]

10 <Example 2>

In Example 2, neutral membranes LFC3 (manufactured by Nitto Denko Corporation) and TML20 (manufactured by Toray Corporation), and anionically charged membranes OFR-625 (manufactured by Organo Corporation) and ES15, ES20 and CPA5 (all manufactured by Nitto Denko Corporation) were used as flat membranes, a stabilized hypobromous acid composition (the composition 1) was used as the antimicrobial agent, and using the flow illustrated in FIG. 1 in a similar manner to Example 1, the permeate concentration was measured using the conditions and method described below.

[0082]

For the test water (water to be treated), a solution prepared by adding the antimicrobial agent to ultra-pure water and then using hydrochloric acid or sodium hydroxide to adjust the pH to 7.0 was used. The concentration of the antimicrobial agent was set to a total chlorine concentration of 10 mg/L. A chiller was used to adjust the water temperature to $25 \pm 1^\circ\text{C}$. The operating pressure for the reverse osmosis membrane was set to 0.75 MPa. The feed water was supplied to the reverse osmosis membrane at 5 L/min. Ammonium chloride was added to the water to be treated in an amount sufficient to produce an ammonia concentration of 0, 0.1, 0.5, 1, 5 or 10 mg/L, and after supplying the water for about 3 hours, the antimicrobial agent concentration (total chlorine concentration) of the water being treated and the permeate were measured, and the permeation rate was calculated. The results are shown in Table 3 and FIG. 2.

[0083]

[Table 3]

	Membrane model	Zeta potential [-mV]	Surface charge	Antimicrobial agent concentration (total chlorine): 10 mg/L					
				Ammonia concentration (mg/L)					
				0	0.1	0.5	1	5	10
				Ammonia/Antimicrobial agent (total chlorine) concentration ratio (-)					
				0	0.01	0.05	0.1	0.5	1
Total chlorine permeation rate (%)	ES15	-35	anionic membrane	0.7	1.5	3.9	6.6	16.6	18.2
	ES20		anionic membrane	1.3	1.7	3.7	4.8	9.2	10.1
	LFC3	-1.3	neutral membrane	0.1	0.2	0.1	0.5	1.2	5.1
	OFR625	-7.9	anionic membrane	0.4	0.8	1.5	2.5	10.0	10.9
	TML20	-3.9	neutral membrane	0.6	1.7	3.7	3.7	7.2	7.5
	CPA5	-20	anionic membrane	0.2	0.6	2.3	3.5	7.4	11.8

[0084]

In this manner, it was evident that compared with the cases where a neutral membrane was used, the cases where an anionically charged membrane was used exhibited a higher antimicrobial agent permeation rate, enabling better suppression of slime contamination even on the secondary side of the reverse osmosis membrane.

[0085]

As described above, by using the method of Example 1, slime contamination was suppressed even on the secondary side of the reverse osmosis membrane, and oxidative deterioration of the reverse osmosis membrane was able to be suppressed.

CLAIMS

1. A water treatment method using a reverse osmosis membrane, in which a water to be treated is treated using the reverse osmosis membrane, wherein
an antimicrobial agent comprising a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound is introduced into the water to be treated, which contains ammonia; and
the reverse osmosis membrane is an anionically charged membrane.
2. A water treatment method using a reverse osmosis membrane, in which a water to be treated is treated using the reverse osmosis membrane, wherein
an antimicrobial agent comprising bromine and a sulfamic acid compound is introduced into the water to be treated, which contains ammonia; and
the reverse osmosis membrane is an anionically charged membrane.
3. The water treatment method using a reverse osmosis membrane according to Claim 1 or 2, wherein
a concentration of the antimicrobial agent or a concentration of the ammonia is adjusted so that a ratio of the concentration of the ammonia relative to a total chlorine concentration in the water to be treated falls within a range from 0.01 to 1.
4. The water treatment method using a reverse osmosis membrane according to Claim 1 or 2, wherein
the water to be treated comprises at least 0.5 mg/L of organic matter that permeates through the reverse osmosis membrane.
5. The water treatment method using a reverse osmosis membrane according to Claim 1 or 2, wherein

the antimicrobial agent is added and introduced into the water to be treated only when a permeate is not used at a use point.