

DESCRIPTION

WATER TREATMENT METHOD USING REVERSE OSMOSIS MEMBRANE, AND WATER TREATMENT APPARATUS

5

TECHNICAL FIELD

[0001]

The present invention relates to a water treatment method and a water treatment apparatus that use 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 general. Chlorine-based oxidizing agents such as hypochlorous acid and the like are representative antimicrobial agents, and are generally 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 introduced into the reverse osmosis membrane intermittently.

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[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 a water to be treated by a reverse osmosis membrane (see Patent 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

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oxidizing agent, and a sulfamic acid compound to a 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

PATENT LITERATURE

[0005]

Patent Document 1: JP 2006-263510 A

Patent Document 2: JP 2015-062889 A

SUMMARY

TECHNICAL PROBLEM

[0006]

However, it was found that in those cases where the water to be treated contained ammonia (ammonium ions), a portion of antimicrobial agents containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound tends to permeate through the reverse osmosis membrane. Because permeation of the antimicrobial agent through the reverse osmosis membrane can lead to a deterioration in the treated water quality and a degradation of the equipment at subsequent stages, it is desirable that such permeation is suppressed.

[0007]

An object of the present invention is to provide a method and an apparatus which, when used in a water treatment for treating, with a reverse osmosis membrane, a water to be

treated that contains ammonia, suppress permeation through the reverse osmosis membrane of antimicrobial agents containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound permeate.

5 SOLUTION TO PROBLEM

[0008]

The present invention provides a water treatment method using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, 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
10 be treated, and the reverse osmosis membrane is a neutral membrane or a cationically charged membrane.

[0009]

Further, the present invention also provides a water treatment method using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated
15 containing ammonia, wherein an antimicrobial agent containing bromine and a sulfamic acid compound is introduced into the water to be treated, and the reverse osmosis membrane is a neutral membrane or a cationically charged membrane.

[0010]

20 In the water treatment method using a reverse osmosis membrane described above, the ammonium ion concentration in the water to be treated is preferably at least 1 mg/L.

[0011]

In the water treatment method using a reverse osmosis membrane described above, it is preferable that the amount of ammonia in the water to be treated containing ammonia is
25 reduced, and the antimicrobial agent is then introduced into the ammonia-reduced water in which the amount of ammonia has been reduced.

[0012]

In the water treatment method using a reverse osmosis membrane described above, the ammonia concentration of the ammonia-reduced water is preferably not more than 5 mg/L.

[0013]

5 In the water treatment method using a reverse osmosis membrane described above, the ammonia in the water to be treated containing ammonia is preferably reduced by an ammonia stripping treatment.

[0014]

10 In the water treatment method using a reverse osmosis membrane described above, the ammonia in the water to be treated containing ammonia is preferably reduced by an ammonia decomposition treatment using an oxidizing agent.

[0015]

15 Further, the present invention also provides a water treatment apparatus using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, 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, and the reverse osmosis membrane is a neutral membrane or a cationically charged membrane.

[0016]

20 Furthermore, the present invention also provides a water treatment apparatus using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, wherein an antimicrobial agent containing bromine and a sulfamic acid compound is introduced into the water to be treated, and the reverse osmosis membrane is a neutral membrane or a cationically charged membrane.

[0017]

25 In the water treatment apparatus using a reverse osmosis membrane described above, the ammonium ion concentration in the water to be treated is preferably at least 1 mg/L.

[0018]

The water treatment apparatus using a reverse osmosis membrane described above preferably includes an ammonia reduction unit that reduces the amount of ammonia in the water to be treated containing ammonia, wherein the antimicrobial agent is introduced into the ammonia-reduced water in which the amount of ammonia has been reduced by the ammonia reduction unit.

[0019]

In the water treatment apparatus using a reverse osmosis membrane described above, the ammonia concentration of the ammonia-reduced water is preferably not more than 5 mg/L.

[0020]

The water treatment apparatus using a reverse osmosis membrane described above preferably includes an ammonia stripping treatment device as the ammonia reduction unit mentioned above.

[0021]

The water treatment apparatus using a reverse osmosis membrane described above preferably includes an ammonia decomposition treatment unit using an oxidizing agent as the ammonia reduction unit mentioned above.

ADVANTAGEOUS EFFECTS OF INVENTION

[0022]

In the present invention, in a water treatment method and a water treatment apparatus for treating, with a reverse osmosis membrane, a water to be treated containing ammonia, permeation through the reverse osmosis membrane of an antimicrobial agent containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound can be suppressed.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

FIG. 1 is a schematic structural diagram illustrating one example of a water treatment system applying a water treatment method using a reverse osmosis membrane according to an embodiment of the present invention.

5 FIG. 2 is a schematic structural diagram of a flat membrane test device used in evaluating the rejection rate at a reverse osmosis membrane in the examples and comparative examples.

FIG. 3 is a diagram illustrating the antimicrobial agent permeation rate (%) relative to the membrane surface zeta potential (-mV) in Example 1 and Comparative Example 1.

10 FIG. 4 is a diagram illustrating the antimicrobial agent permeation rate (%) relative to the ammonium ion concentration (mg/L) in Example 2 and Comparative Example 2.

FIG. 5 is a diagram illustrating the antimicrobial agent permeation rate (%) relative to the ammonium ion concentration (mg/L) in Example 3 and Comparative Example 3.

15 FIG. 6 is a schematic structural diagram illustrating one example of a water treatment apparatus using a reverse osmosis membrane according to an embodiment of the present invention.

FIG. 7 is a schematic structural diagram illustrating one example of a water treatment system applying a water treatment apparatus using a reverse osmosis membrane according to an embodiment of the present invention.

20 FIG. 8 is a diagram illustrating the antimicrobial agent permeation rate (%) relative to the ammonium ion concentration (mg/L) in Example 4-1.

FIG. 9 is a diagram illustrating the antimicrobial agent permeation rate (%) relative to the ammonium ion concentration (mg/L) in Example 4-2.

25 FIG. 10 is a schematic structural diagram of a pilot apparatus used for evaluating the permeation rates of antimicrobial agents in Examples 5 to 8.

DESCRIPTION OF EMBODIMENTS

[0024]

Embodiments of the present invention are described below. These embodiments are merely examples of implementing the present invention, and the present invention is in no way limited by these embodiments.

5 [0025]

<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 using a neutral membrane or a cationically charged membrane as the reverse osmosis membrane in which an antimicrobial agent
10 containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound is introduced 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
15 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"
20 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".

[0026]

In other words, the water treatment method using a reverse osmosis membrane
25 according to an embodiment of the present invention is a method for treating, with a reverse osmosis membrane, a water to be treated containing ammonia, 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 the

water to be treated, and a neutral membrane or a cationically charged membrane is used as the reverse osmosis membrane. As a result, it is thought that a stabilized hypobromous acid composition or a stabilized hypochlorous acid composition can be produced within the water being treated.

5 [0027]

Further, the water treatment method using a reverse osmosis membrane according to another embodiment of the present invention is a method for treating, with a reverse osmosis membrane, a water to be treated containing ammonia, wherein a stabilized hypobromous acid composition that is a "reaction product of a bromine-based oxidizing agent and a
10 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" may be introduced into the water to be treated, and a neutral membrane or a cationically charged membrane is used as the reverse osmosis membrane.

[0028]

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

25 [0029]

Further, the water treatment method using a reverse osmosis membrane according to another embodiment of the present invention is a method for treating, with a reverse osmosis membrane, a water to be treated containing ammonia, 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 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 the water to be treated, and a neutral membrane or a cationically charged membrane is used as the reverse osmosis membrane. Alternatively, the water treatment method may be a method wherein 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, and a neutral membrane or a cationically charged membrane is used as the reverse osmosis membrane.

[0030]

As a result of intensive investigation, the inventors of the present invention discovered that when a water to be treated contains ammonia, the charge of the reverse osmosis membrane that is used changes the permeation rate of the antimicrobial agent through the membrane. Generally, many reverse osmosis membranes are negatively charged, but it was found that as the charge of the membrane approached a neutral charge, the permeation rate of antimicrobial agents decreased. When an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound is introduced into a water to be treated containing ammonia, by using a neutral membrane or a cationically charged membrane as the reverse osmosis membrane, the permeation of the antimicrobial agent through the reverse osmosis membrane can be suppressed.

[0031]

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 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
5 embodiment of the present invention functions favorably as a slime inhibitor for use in a water treatment method for treating, with a reverse osmosis membrane, a water to be treated containing ammonia.

[0032]

Among the water treatment methods using a reverse osmosis membrane according to
10 embodiments of the present invention, in the case of an "antimicrobial agent containing a 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 small. When a chlorine-based oxidizing agent is included, the production of chloric acid may be a concern.

15 [0033]

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 may be remarkably low.

20 [0034]

In the water treatment method using a reverse osmosis membrane according to an embodiment 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 containing ammonia using a chemical feed pump or the
25 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.

[0035]

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 containing ammonia using a chemical feed pump or the like.

5 [0036]

In the water treatment method using a reverse osmosis membrane according to an embodiment 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
10 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.

15 [0037]

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 effect may sometimes be unobtainable, whereas if the concentration is greater than 100 mg/L, then there
20 is a possibility that deterioration of the reverse osmosis membrane or corrosion of the lines or the like may occur.

[0038]

In the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, the ammonium ion concentration in the water to be
25 treated is preferably at least 1 mg/L, and more preferably 5 mg/L or greater. When the ammonium ion concentration in the water to be treated is at least 1 mg/L, the change in the permeation rate of the antimicrobial agent due to the membrane charge tends to increase, and when the ammonium ion concentration in the water to be treated is 5 mg/L or greater, the

difference in the permeation rate of the antimicrobial agent due to the membrane charge may be particularly large.

[0039]

5 The ratio of the ammonia concentration relative to the total chlorine concentration in the water to be treated (ammonia concentration (mg/L) / antimicrobial agent concentration (total chlorine concentration: mg/L)) is, for example, within a range from 0.01 to 50, and is preferably within a range from 0.01 to 1.0. If the ratio of the ammonia concentration relative to the total chlorine concentration in the water to be treated is less than 0.01 or greater than 1.0, then the difference in the antimicrobial agent permeation rates for
10 anionically charge membranes, and neutral membranes and cationically charged membranes, may sometimes decrease.

[0040]

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.

[0041]

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 particularly preferred as slime inhibitors for reverse osmosis membranes.

25 [0042]

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

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

[0043]

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.

[0044]

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
15 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 alone, or a
20 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.

[0045]

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

25 R_2NSO_3H (1)

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

[0046]

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 alkyl group having 1 to 8 carbon atoms, such as N-methylsulfamic acid, N-ethylsulfamic acid,

5 N-propylsulfamic acid, N-isopropylsulfamic acid and N-butylsulfamic acid, sulfamic acid compounds in which the two R groups are both alkyl groups having 1 to 8 carbon atoms, such as N,N-dimethylsulfamic acid, N,N-diethylsulfamic acid, N,N-dipropylsulfamic acid, N,N-dibutylsulfamic acid, 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
10 the other is an aryl group having 6 to 10 carbon atoms, 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 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.
15 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 impact and the like, the use of sulfamic acid (amidosulfuric acid) as the sulfamic acid compound is preferred.

[0047]

In the water treatment method using a reverse osmosis membrane according to an
20 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. 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.

25 [0048]

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 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 may be almost non-existent, even for polyamide-based polymer membranes.

[0049]

Reverse osmosis membranes include neutral membranes, anionically charged membranes and cationically charged membranes. In this description, a neutral membrane is defined as a membrane for which the zeta potential at pH 7.0, measured using the zeta potential measurement method described below in the examples, is at least -10 mV but less than 5 mV, a cationically charged membrane is defined as a membrane for which the zeta potential is 5 mV or greater, and an anionically charged membrane is defined as a membrane for which the zeta potential is less than -10 mV. The zeta potential of a neutral membrane is preferably at least -5 mV, more preferably at least -3.9 mV, and even more preferably -1.3 mV or greater. Although there are no particular limitations on the upper limit for the zeta potential of a cationically charged membrane, the zeta potential is, for example, not more than 20 mV.

[0050]

In the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, by using a neutral membrane or a cationically charged membrane as the reverse osmosis membrane, permeation through the reverse osmosis membrane of the antimicrobial agent containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound can be better suppressed compared with those cases where an anionically charged membrane is used.

[0051]

Examples of commercially available neutral membranes include BW30XFR (manufactured by The Dow Chemical Company), LFC3 (manufactured by Nitto Denko

Corporation), TML20 (manufactured by Toray Industries, Inc.), and OFR625 (manufactured by Organo Corporation).

[0052]

Examples of commercially available cationically charged membranes include ES10C
5 (manufactured by Nitto Denko Corporation) and the like.

[0053]

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

10 [0054]

In the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, the water to be treated that is supplied to the reverse osmosis membrane treatment 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.

15 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 treated, there are no particular limitations, provided the pH does not exceed the general applicable 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
20 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 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
25 permeate can be ensured, while achieving a satisfactory slime suppression effect.

[0055]

In those cases where scale develops in the reverse osmosis membrane treatment 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. 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.

[0056]

Further, one method for suppressing the occurrence of scale without using a dispersant involves, for example, adjusting the operating conditions for the reverse osmosis membrane treatment 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.

[0057]

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

[0058]

It is thought that the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention is particularly suited to applications to wastewater recovery, for example, recovery of wastewater from the electronics industry. Electronics industry wastewater frequently contains low-molecular weight organic matter, and one possible flow for the wastewater recovery is the type of flow illustrated in FIG. 1, which includes a reverse osmosis membrane treatment system 26, which contains a reverse osmosis membrane treatment device 22 as a water treatment apparatus for applying the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, provided at a subsequent stage to a biological treatment system 16 containing a biological treatment device 10 and a membrane treatment device 14.

[0059]

A water treatment system 1 illustrated in FIG. 1 contains the biological treatment device 10 as a biological treatment unit, a biologically treated water tank 12, the membrane

treatment device 14 as a membrane treatment unit, a membrane treated water tank 18, and the reverse osmosis membrane treatment system 26 as a water treatment apparatus using a reverse osmosis membrane. The reverse osmosis membrane treatment system 26 contains the reverse osmosis membrane treatment device 22 having a neutral membrane or a cationically charged membrane as a reverse osmosis membrane treatment unit. The reverse osmosis membrane treatment system 26 may also contain a treatment water tank 20 for storing the water to be treated, and a second reverse osmosis membrane treatment device 24 that functions as a second reverse osmosis membrane treatment unit.

[0060]

In the water treatment system 1, a raw water such as an electronics industry wastewater is fed into the biological treatment device 10, and a biological treatment is performed in the biological treatment device 10 (biological treatment step). The biologically treated water that has undergone the biological treatment may be stored as necessary in the biologically treated water tank 12, and is then fed into the membrane treatment device 14, where a membrane treatment (clarification) is performed using a clarification membrane (membrane treatment step). The membrane treated water that has undergone the membrane treatment may be stored as necessary in the membrane treated water tank 18, and is then fed into, and stored in, the treatment water tank 20 of the reverse osmosis membrane treatment system 26 as a water to be treated. This water to be treated is fed from the treatment water tank 20 to the reverse osmosis membrane treatment device 22, and the neutral membrane or cationically charged membrane in the reverse osmosis membrane treatment device 22 is used to perform a reverse osmosis membrane treatment (reverse osmosis membrane treatment step). The permeate obtained in the reverse osmosis membrane treatment is discharged from the system. The concentrate may be either discharged from the system, or if necessary, may be fed into the second reverse osmosis membrane treatment device 24, with a second reverse osmosis membrane treatment then being performed in the second reverse osmosis membrane treatment device 24 (second reverse osmosis membrane treatment step). The concentrate obtained in the second reverse

osmosis membrane treatment is discharged from the system. The permeate may by either discharged from the system, or if necessary, may be fed into the treatment water tank 20 and recirculated.

[0061]

5 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, but the antimicrobial agent may be added to at least one of the biologically treated water tank 12, the membrane treated water tank 18, and the treatment water tank 20. The antimicrobial agent may also be added to at least one of the line connecting the biological
10 treatment device 10 and the biologically treated water tank 12, the line connecting the biologically treated water tank 12 and the membrane treatment device 14, the line connecting the membrane treatment device 14 and the membrane treated water tank 18, the line connecting the membrane treated water tank 18 and the treatment water tank 20, and the line connecting the treatment water tank 20 and the reverse osmosis membrane treatment
15 device 22. In terms of cost and the like, the most advantageous methods involve addition to the treatment water tank 20, addition to the line connecting the membrane treated water tank 18 and the treatment water tank 20, or addition to the line connecting the treatment water tank 20 and the reverse osmosis membrane treatment device 22. In those cases where slime generation is confirmed at the membrane treated water tank 18, prior to concentration by the
20 reverse osmosis membrane of the reverse osmosis membrane treatment device 22, the antimicrobial agent may be added to the membrane treated water tank 18 or the lines either side thereof, but because the membrane treated water in the membrane treated water tank 18 is frequently used for backwashing of the membrane treatment device 14, a portion of the added antimicrobial agent may be often wasted. In those cases where the antimicrobial
25 agent is added to the biologically treated water tank 12 or the lines either side thereof, consumption of the antimicrobial agent components by suspended organic matter produced following the biological treatment means the amount added of the antimicrobial agent may

be increased, leading to an increase in running costs, and therefore this method may be employed only when a slime generation risk exists throughout the entire system.

[0062]

The water treatment system 1 of FIG. 1 illustrates an example of a biological treatment system 16 that contains the biological treatment device 10, the biologically treated water tank 12 and the membrane treatment device 14 as separate devices, but a membrane separation activated sludge device (MBR) that combines these devices into a single unit may also be used.

[0063]

In the water treatment system 1 of FIG. 1, low-molecular weight organic matter and the like contained in the raw water is decomposed by the biological treatment, microbial metabolites and the like are rejected by the membrane treatment device 14 containing the clarification membrane and the like, and various ions and any residual organic matter and the like are then rejected by the neutral membrane or the cationically charged membrane of the reverse osmosis membrane treatment device 22, thus obtaining a treated water (permeate). In this type of wastewater recovery, ammonia may be contained in the wastewater itself, and ammonia may be also often generated by the biological treatment. For example, when a wastewater containing tetramethylammonium hydroxide as an organic substance is subjected to a biological treatment, ammonia tends to be readily produced.

[0064]

At this time, biofouling of the latter-stage clarification membrane and reverse osmosis membrane by microbial metabolites generated by the biological treatment and residual low-molecular weight organic matter that remains even after the biological treatment may be a concern. Dealing with this concern by using hypochlorous acid which exhibits a powerful sterilizing action is one possible countermeasure, but hypochlorous acid may sometimes cause degradation of the polyamide-based reverse osmosis membranes that have become mainstream in recent years. Providing an activated carbon column or a reducing agent injection point at a stage prior to the reverse osmosis membrane are also possibilities, but in

either case, the initial running costs tend to be problematic. Accordingly, in the water treatment system 1, by introducing an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound into the water to be treated containing ammonia, not only may be a powerful sterilizing function
5 obtained, but oxidative deterioration of polyamide-based reverse osmosis membranes may be unlikely and the rejection rate by the reverse osmosis membrane may be high, meaning there may be little effect on the quality of the latter-stage treated water (permeate).

[0065]

When the antimicrobial agent is added in this manner, if the antimicrobial agent
10 permeates through to the treated water side, then deterioration in the treated water quality may become a problem. Accordingly, in the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, by using a neutral membrane or a cationically charged membrane as the reverse osmosis membrane in the reverse osmosis membrane treatment device 22, permeation of the antimicrobial agent
15 through the reverse osmosis membrane can be suppressed, with almost no antimicrobial agent detected in the permeate.

[0066]

Further, at this time, the pH of the water to be treated that is supplied to the reverse osmosis membrane treatment device 22, namely the operating pH of the reverse osmosis
20 membrane treatment device 22, is preferably 9 or lower. Under alkali conditions exceeding a pH of 9, the salt rejection rate of the reverse osmosis membrane may sometimes worsen, and the oxidizing power of the antimicrobial agent may sometimes deteriorate. Provided the pH of the water to be treated that is supplied to the reverse osmosis membrane treatment device 22 is 9 or lower, the water quality of the RO permeate can be more favorably
25 maintained, and slime generation can be better suppressed.

[0067]

In a wastewater recovery flow such as that of the water treatment system 1, the second reverse osmosis membrane treatment device 24 (brine RO) is generally provided to increase

the water recovery ratio. The second reverse osmosis membrane treatment device 24 receives the concentrate from the reverse osmosis membrane treatment device 22 as a raw water, returns the resulting permeate to the treatment water tank 20, and discharges the concentrate from the system. There is also a risk of slime generation in the second reverse osmosis membrane treatment device 24, but if the permeation rate of the antimicrobial agent through the reverse osmosis membrane treatment device 22 is low, then the antimicrobial agent components may be retained in the raw water supplied to the second reverse osmosis membrane treatment device 24. By using a neutral membrane or a cationically charged membrane as the reverse osmosis membrane in the reverse osmosis membrane treatment device 22, large amounts of the antimicrobial agent components may be retained in the raw water for the second reverse osmosis membrane treatment device 24, meaning slime generation in the second reverse osmosis membrane treatment device 24 can be suppressed.

[0068]

In the water treatment system 1 of FIG. 1, a biological treatment was described as an example of a pretreatment prior to the reverse osmosis membrane treatment, but in the pretreatment step performed prior to the reverse osmosis membrane treatment, any biological, physical or chemical pretreatment such as a biological treatment, flocculation treatment, flocculation sedimentation treatment, pressure flotation treatment, filtration treatment, membrane separation treatment, activated carbon treatment, ozone treatment or ultraviolet irradiation treatment, or any combination of two or more of these treatments, may be performed as required.

[0069]

In the reverse osmosis membrane treatment system 26, in addition to the reverse osmosis membranes, the system may also include a pump, safety filter, flow rate measurement device, pressure measurement device, temperature measurement device, oxidation-reduction potential (ORP) measurement device, residual chlorine measurement device, electrical conductivity measurement device, pH measurement device, and/or energy recovery device or the like as required.

[0070]

In the water treatment system 1, if necessary, pH adjusters and scale inhibitors other than the stabilized hypobromous acid composition or stabilized hypochlorous acid composition may be added to at least one of the biologically treated water, the membrane
5 treated water and the water to be treated in at least one location among the biologically treated water tank 12 and the lines either side thereof, the membrane treated water tank 18 and the lines either side thereof, and the treatment water tank 20 and the lines either side thereof.

[0071]

10 An outline of one example of a water treatment apparatus using a reverse osmosis membrane according to an embodiment of the present invention is illustrated in FIG. 6, and the structure of that apparatus is described below.

[0072]

A water treatment apparatus 3 illustrated in FIG. 6 contains an ammonia reduction
15 device 30 as an ammonia reduction unit for reducing the amount of ammonia in a water to be treated containing ammonia, and a reverse osmosis membrane treatment device 34 having a neutral membrane or a cationically charged membrane as a reverse osmosis membrane treatment unit. The water treatment apparatus 3 may also include an ammonia-reduced water tank 32 for storing the ammonia-reduced water.

20 [0073]

In the water treatment apparatus 3, a water to be treated line 36 is connected to an inlet of the ammonia reduction device 30. An outlet from the ammonia reduction device 30 and an inlet of the ammonia-reduced water tank 32 are connected via an ammonia-reduced water line 38. An outlet from the ammonia-reduced water tank 32 and an inlet of the reverse
25 osmosis membrane treatment device 34 are connected via an antimicrobial agent-containing water line 40. A permeate line 42 is connected to a permeate outlet from the reverse osmosis membrane treatment device 34, and a concentrate line 44 is connected to a

concentrate outlet. An antimicrobial agent addition line 46 is connected to the ammonia-reduced water tank 32.

[0074]

The water treatment method according to an embodiment of the present invention and the operation of the water treatment apparatus 3 are described below.

[0075]

In the water treatment apparatus 3, a water to be treated containing ammonia (ammonium ions) is supplied to the ammonia reduction device 30 through the water to be treated line 36, and the amount of ammonia can be reduced in the ammonia reduction device 30 (ammonia reduction step).

[0076]

The ammonia-reduced water obtained following ammonia reduction by the ammonia reduction device 30 is passed through the ammonia-reduced water line 38, and if necessary, is fed into the ammonia-reduced water tank 32 and stored. An antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound is added and introduced into the ammonia-reduced water in the ammonia-reduced water tank 32 (antimicrobial agent addition step). The antimicrobial agent may also be added to the ammonia-reduced water line 38 or to the antimicrobial agent-containing water line 40.

[0077]

The antimicrobial agent-containing water into which the antimicrobial agent has been introduced is supplied to the reverse osmosis membrane treatment device 34 through the antimicrobial agent-containing water line 40, and a reverse osmosis membrane treatment is performed in the reverse osmosis membrane treatment device 34 (reverse osmosis membrane treatment step). The permeate obtained from the reverse osmosis membrane treatment is discharged through the permeate line 42 as treated water, and the concentrate is discharged through the concentrate line 44.

[0078]

As a result of repeated investigation, the inventors of the present invention discovered that the permeation rate of an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound increased in accordance with the ammonia concentration in the water to be treated. Accordingly, by
5 reducing the ammonia concentration in the water to be treated as a pretreatment prior to the reverse osmosis membrane treatment, permeation through the reverse osmosis membrane of the antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound could be suppressed. When the ammonia concentration in the ammonia-reduced water was not more than 5 mg/L, the reduction effect
10 on the antimicrobial agent permeation rate achieved as a result of the ammonia reduction could be particularly effective.

[0079]

There are no particular limitations on the ammonia reduction device 30, provided it is capable of reducing the amount of ammonia (ammonium ions) in the water to be treated.

15 Examples of the ammonia reduction device 30 include an ammonia stripping treatment device that performs an ammonia stripping treatment, an ammonia decomposition treatment device that performs an ammonia decomposition treatment using an oxidizing agent, and a pretreatment that uses a reverse osmosis membrane. Among these, in terms of yielding almost no increase in the risk of slime, and enabling the same chemicals as the antimicrobial
20 agent used in a later stage to be used as the oxidizing agent, thereby not increasing the types of chemicals that must be used, an ammonia stripping treatment device that performs an ammonia stripping treatment and an ammonia decomposition treatment device that performs an ammonia decomposition treatment using an oxidizing agent are preferred.

[0080]

25 An ammonia stripping treatment is a treatment method in which an alkali solution is added to the ammonia-containing water, and following heating, the water is passed through a stripper packed with a filler and brought into contact with steam and air, thereby causing the ammonia in the ammonia-containing water to migrate into the gas phase.

[0081]

The ammonia stripping treatment device is, for example, a distillation column inside which a perforated panel or a filler or the like has been installed, and the ammonia-containing water is introduced from the upper section of the distillation column while steam is blown in from the lower section of the column, and by bringing the ammonia-containing water and the steam into contact, the free ammonia in the ammonia-containing water can be forced out of the water into the steam side. The ammonia gas that has been forced out in this manner may also be subjected to a decomposition treatment. Examples of this ammonia gas decomposition treatment include a method in which the ammonia gas is passed through a catalytic reaction column packed with a catalyst, thereby converting the ammonia gas to harmless nitrogen, and a method in which the ammonia gas is reacted with sulfuric acid to produce ammonium sulfate, but the ammonia gas may also be collected and reused as ammonia water.

[0082]

The pH in the ammonia stripping treatment is preferably 10 or higher, more preferably 10.5 or higher, and even more preferably within a range from 10.5 to 12. If the pH in the ammonia stripping treatment is less than 10, then the fraction of free ammonia (NH_3) decreases, and the ammonia removal efficiency may sometimes deteriorate. If the pH in the ammonia stripping treatment exceeds 12, then problems may arise, including the possibility of degradation of the perforated panel or filler inside the distillation column during the ammonia stripping treatment, and an increase in the cost of the alkali chemical.

[0083]

The efficiency of the ammonia stripping treatment increases with increasing temperature, and therefore the water temperature is generally increased to a value within a range from 40°C to 100°C, and preferably a temperature within a range from 80°C to 100°C, using steam.

[0084]

Examples of the oxidizing agent that may be used in the ammonia decomposition treatment using an oxidizing agent include chlorine-based oxidizing agents, bromine-based oxidizing agents, stabilized hypobromous acid compositions containing a bromine-based oxidizing agent and a sulfamic acid compound, and stabilized hypochlorous acid compositions containing a chlorine-based oxidizing agent and a sulfamic acid compound, and of these, stabilized hypobromous acid compositions and stabilized hypochlorous acid compositions are preferred. Examples of the chlorine-based oxidizing agents, bromine-based oxidizing agents, stabilized hypobromous acid compositions and stabilized hypochlorous acid compositions include the same materials as the chlorine-based oxidizing agents, bromine-based oxidizing agents, stabilized hypobromous acid compositions and stabilized hypochlorous acid compositions described below. The oxidizing agent used in the ammonia decomposition treatment is preferably the same material as the antimicrobial agent that is introduced into the ammonia-reduced water in the latter stages after the ammonia reduction step. By using the same oxidizing agent as the antimicrobial agent that is introduced into the ammonia-reduced water, and using the oxidizing agent in an amount greater than that required for the ammonia decomposition, the oxidizing agent that remains following the ammonia decomposition treatment can function as the antimicrobial agent in the latter-stage reverse osmosis membrane treatment device.

[0085]

The amount of the oxidizing agent used in the ammonia decomposition treatment is set so that the ratio of the molar concentration of effective halogen, calculated as an effective chlorine concentration, relative to the molar concentration of ammoniacal nitrogen ($\text{NH}_4\text{-N}$) in the water to be treated, is preferably at least 1.6, and more preferably 2.0 or greater. The larger this ratio becomes, the greater the ammonia reduction effect may become. By ensuring that the ratio of the molar concentration of effective halogen, calculated as an effective chlorine concentration, relative to the molar concentration of ammoniacal nitrogen in the water to be treated is 2.0 or greater, the residual oxidizing agent from the ammonia decomposition treatment is able to function as an antimicrobial agent in the latter-stage

reverse osmosis membrane treatment device. The upper limit for this molar concentration ratio is, for example, not more than 100.

[0086]

The pH in the ammonia decomposition treatment using an oxidizing agent is, for example, within a range from 3 to 10, and preferably within a range from 4 to 9. If the pH in the ammonia decomposition treatment is less than 3, then the ammoniacal nitrogen decomposition effect may sometimes deteriorate, whereas if the pH exceeds 10, then an increase in the rejection rate of the latter-stage reverse osmosis membrane may sometimes require the pH to be adjusted to a more neutral setting.

[0087]

The temperature during the ammonia decomposition treatment using an oxidizing agent is, for example, within a range from 0°C to 100°C, and preferably within a range from 0°C to 40°C. If the temperature in the ammonia decomposition treatment is less than 0°C, then the treated water may sometimes freeze, whereas if the temperature exceeds 100°C, the oxidizing agent or the ammonia may volatilize, causing a deterioration in the ammonia decomposition efficiency.

[0088]

The ammonia concentration in the water to be treated in the ammonia reduction step is, for example, within a range from 0.1 mg/L to 500 mg/L, and is preferably within a range from 0.1 mg/L to 30 mg/L.

[0089]

In the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, the antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound is introduced into the ammonia-reduced water obtained by reducing the amount of ammonia using the ammonia reduction device 30. 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".

10 [0090]

In other words, in the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, 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" may be introduced into the ammonia-reduced water. As a result, it is thought that a stabilized hypobromous acid composition or a stabilized hypochlorous acid composition can be produced in the ammonia-reduced water.

[0091]

Further, in the water treatment apparatus and method using a reverse osmosis membrane according to other embodiments of the present invention, 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" may be introduced into the ammonia-reduced water.

25 [0092]

Specifically, in the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, a mixture of "bromine", "bromine chloride", "hypobromous acid" or a "reaction product of sodium bromide and

hypochlorous acid", and a "sulfamic acid compound" is introduced into the ammonia-reduced water. Alternatively, a mixture of "hypochlorous acid" and a "sulfamic acid compound" may be introduced into the ammonia-reduced water.

[0093]

5 Further, in the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, 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 of hypobromous acid and a sulfamic acid compound" or a "reaction product of a sulfamic acid
10 compound with a reaction product of sodium bromide and hypochlorous acid" is introduced into the ammonia-reduced water. Alternatively, a stabilized hypochlorous acid composition that is a "reaction product of hypochlorous acid and a sulfamic acid compound" may be introduced into the ammonia-reduced water.

[0094]

15 In the water treatment apparatus and method using a reverse osmosis membrane according to embodiments 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
20 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 apparatus and method using a reverse osmosis membrane according to embodiments of the present invention functions favorably as a slime
25 inhibitor for use in a water treatment apparatus and method for treating a water to be treated that contains ammonia using a reverse osmosis membrane.

[0095]

Among the various water treatment apparatus and methods using a reverse osmosis membrane according to embodiments of the present invention, in the case of an "antimicrobial agent containing a 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 may be particularly minor. When a chlorine-based oxidizing agent exists, the production of chloric acid may be a concern.

[0096]

Among the various water treatment apparatus and 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 may be remarkably low.

[0097]

In the water treatment apparatus and method 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 ammonia-reduced water 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 ammonia-reduced water, or the neat liquids may be mixed together and then added to the ammonia-reduced water.

[0098]

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 ammonia-reduced water using a chemical feed pump or the like.

[0099]

In the water treatment apparatus and method 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.

[0100]

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 effect may sometimes be unobtainable, 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 lines or the like may occur.

[0101]

In the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, the ammonium ion concentration in the ammonia-reduced water is preferably not more than 5 mg/L, and is more preferably 1 mg/L or less. If the ammonium ion concentration in the ammonia-reduced water exceeds 5 mg/L, then the antimicrobial agent tends to permeate through the reverse osmosis membrane more readily.

[0102]

The ratio of the concentration of ammonia relative to the total chlorine concentration in the ammonia-reduced water (ammonia concentration (mg/L) / antimicrobial agent concentration (total chlorine concentration: mg/L)) is, for example, within a range from 0.01 to 50. If the ratio of the ammonia concentration relative to the total chlorine concentration in the ammonia-reduced water is less than 0.01, then because the antimicrobial agent is satisfactorily rejected by the reverse osmosis membrane, there may be little effect in further reducing the ammonia concentration, whereas if the ratio exceeds 50, then the permeation

rate of the antimicrobial agent may remain quite high even if the ammonia concentration is reduced, and the effect of reducing the permeation rate may not be observed.

[0103]

In the water treatment apparatus and method using a reverse osmosis membrane
5 according to embodiments of the present invention, an alkali may also be introduced into the ammonia-reduced water.

[0104]

In the water treatment apparatus and method using a reverse osmosis membrane
according to embodiments of the present invention, the pH of the ammonia-reduced water
10 that is supplied to the reverse osmosis membrane treatment device containing the reverse osmosis membrane 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 ammonia-reduced water 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 ammonia-reduced water, there are no particular limitations, provided the pH does
15 not exceed the general applicable 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 apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, by performing operations with the pH of
20 the ammonia-reduced water 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 a satisfactory slime suppression effect.

[0105]

25 In those cases where scale develops in the reverse osmosis membrane device when the pH of the ammonia-reduced water is 5.5 or higher, a dispersant may be used in combination with the antimicrobial agent for the purpose of scale suppression. Examples of the dispersant include polyacrylic acid, polymaleic acid, and phosphonic acid and the like. The

amount of the dispersant added to the ammonia-reduced water is, for example, within a range from 0.1 to 1,000 mg/L in terms of the concentration within the RO concentrate.

[0106]

Further, one examples of a method for suppressing scale generation without using a 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 of calcium scale, is not more than 0.

[0107]

The bromine-based oxidizing agent, bromine compound, chlorine-based oxidizing agent, sulfamic acid compound, alkali, and reverse osmosis membrane are all as described above.

[0108]

It is thought that the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention will be particularly suited to application to water recovery, such as the recovery of wastewater from the electronics industry. Electronics industry wastewater frequently contains low-molecular weight organic matter, and one possible flow for the wastewater recovery is the type of flow illustrated in FIG. 7, which includes the water treatment apparatus 3, which contains the ammonia reduction device 30 and the reverse osmosis membrane treatment device 34, and can be used for performing the water treatment method using a reverse osmosis membrane according to an embodiment of the present invention, provided as a subsequent stage to a biological treatment system 56 containing a biological treatment device 50 and a membrane treatment device 54.

[0109]

A water treatment system 5 illustrated in FIG. 7 includes the biological treatment device 50 as a biological treatment unit, a biologically treated water tank 52, the membrane treatment device 54 as a membrane treatment unit, a membrane treated water tank 58, and

the water treatment apparatus 3 described above. The water treatment system 5 may also include a second reverse osmosis membrane device 60 as a second reverse osmosis membrane treatment unit.

[0110]

5 In the water treatment system 5, a raw water such as an electronics industry wastewater is fed into the biological treatment device 50, and a biological treatment is performed in the biological treatment device 50 (biological treatment step). The biologically treated water that has undergone the biological treatment may be stored as necessary in the biologically treated water tank 52, and is then fed into the membrane
10 treatment device 54, where a membrane treatment (clarification) is performed using a clarification membrane (membrane treatment step). The membrane treated water that has undergone the membrane treatment may be stored as necessary in the membrane treated water tank 58, and is then supplied as a water to be treated to the ammonia reduction device 30 of the water treatment apparatus 3, and the amount of ammonia is reduced in the ammonia
15 reduction device 30 (ammonia reduction step).

[0111]

The ammonia-reduced water that has undergone ammonia reduction in the ammonia reduction device 30 is fed into, and stored in, the ammonia-reduced water tank 32 as required. An antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based
20 oxidizing agent and a sulfamic acid compound is added and introduced into the ammonia-reduced water in the ammonia-reduced water tank 32 (antimicrobial agent addition step). The antimicrobial agent may also be added to the lines on either side of the ammonia-reduced water tank 32.

[0112]

25 The antimicrobial agent-containing water into which the antimicrobial agent has been introduced is supplied to the reverse osmosis membrane treatment device 34, and a reverse osmosis membrane treatment is performed in the reverse osmosis membrane treatment device 34 (reverse osmosis membrane treatment step). The permeate obtained from the

reverse osmosis membrane treatment is discharged through a permeate line as treated water, and the concentrate is discharged through a concentrate line. The permeate obtained in the reverse osmosis membrane treatment is discharged from the system. The concentrate may be either discharged from the system, or if necessary, may be fed into the second reverse osmosis membrane treatment device 60, with a second reverse osmosis membrane treatment then being performed in the second reverse osmosis membrane treatment device 60 (second reverse osmosis membrane treatment step). The concentrate obtained in the second reverse osmosis membrane treatment is discharged from the system. The permeate may by either discharged from the system, or if necessary, may be fed into the ammonia-reduced water tank 32 and recirculated.

[0113]

The water treatment system 5 of FIG. 7 illustrates an example of a biological treatment system 56 that contains the biological treatment device 50, the biologically treated water tank 52 and the membrane treatment device 54 as separate devices, but a membrane separation activated sludge device (MBR) that combines these devices into a single unit may also be used.

[0114]

In the water treatment system 5 of FIG. 7, low-molecular weight organic matter and the like contained in the raw water is decomposed by the biological treatment, microbial metabolites and the like are rejected by the membrane treatment device 54 containing the clarification membrane and the like, the amount of ammonia is then reduced in the ammonia reduction device 30, and various ions and any residual organic matter and the like are then rejected by the reverse osmosis membrane treatment device 34, thus obtaining a treated water (permeate). In this type of wastewater recovery, ammonia may be contained in the wastewater itself, and ammonia is also often generated by the biological treatment. For example, when a wastewater containing tetramethylammonium hydroxide as an organic substance is subjected to a biological treatment, ammonia tends to be readily produced.

[0115]

At this time, biofouling of the latter-stage reverse osmosis membrane by microbial metabolites generated by the biological treatment and residual low-molecular weight organic matter that remains even after the biological treatment may be a concern. Dealing with this concern by using hypochlorous acid which exhibits a powerful sterilizing action is one possible countermeasure, but hypochlorous acid may sometimes cause degradation of the polyamide-based reverse osmosis membranes that have become mainstream in recent years. Providing an activated carbon column or a reducing agent injection point at a stage prior to the reverse osmosis membrane are also possibilities, but in either case, the initial running costs tend to be problematic. Accordingly, in the water treatment system 5, by reducing the amount of ammonia in the ammonia reduction device, and then introducing an antimicrobial agent containing a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound into the ammonia-reduced water, not only may be a powerful sterilizing function obtained, but oxidative deterioration of polyamide-based reverse osmosis membranes may be unlikely and the rejection rate by the reverse osmosis membrane may be high, meaning there may be little effect on the quality of the latter-stage treated water (permeate).

[0116]

When the antimicrobial agent is added in this manner, if the antimicrobial agent permeates through to the treated water side, then deterioration in the treated water quality may become a problem. Accordingly, in the water treatment apparatus and method using a reverse osmosis membrane according to embodiments of the present invention, by reducing the ammonia concentration in the water to be treated as a pretreatment prior to the reverse osmosis membrane treatment, permeation of the antimicrobial agent through the reverse osmosis membrane can be suppressed, with almost no antimicrobial agent detected in the permeate.

[0117]

Further, at this time, the pH of the ammonia-reduced water that is supplied to the reverse osmosis membrane treatment device 34, namely the operating pH of the reverse

osmosis membrane treatment device 34, is preferably 9 or lower. Under alkali conditions exceeding a pH of 9, the salt rejection rate of the reverse osmosis membrane may sometimes worsen, and the oxidizing power of the antimicrobial agent may sometimes deteriorate.

Provided the pH of the ammonia-reduced water supplied to the reverse osmosis membrane treatment device 34 is 9 or lower, the water quality of the RO permeate can be more favorably maintained, and slime generation can be better suppressed.

[0118]

In a wastewater recovery flow such as that of the water treatment system 5, the second reverse osmosis membrane treatment device 60 (brine RO) is generally provided to increase the water recovery ratio. The second reverse osmosis membrane treatment device 60 receives the concentrate from the reverse osmosis membrane treatment device 34 as a raw water, returns the resulting permeate to the ammonia-reduced water tank 32, and discharges the concentrate from the system. There is also a risk of slime generation in the second reverse osmosis membrane treatment device 60, but if the permeation rate of the

antimicrobial agent through the reverse osmosis membrane treatment device 34 is low, then the antimicrobial agent components may be retained in the raw water supplied to the second reverse osmosis membrane treatment device 60. Because large amounts of the antimicrobial agent components are retained in the raw water for the second reverse osmosis membrane treatment device 60, slime generation in the second reverse osmosis membrane treatment device 60 can be suppressed.

[0119]

In the water treatment system 5 of FIG. 7, a biological treatment was described as an example of a pretreatment prior to the reverse osmosis membrane treatment, but in the pretreatment step performed prior to the reverse osmosis membrane treatment, any biological, physical or chemical pretreatment such as a biological treatment, flocculation treatment, flocculation sedimentation treatment, pressure flotation treatment, filtration treatment, membrane separation treatment, activated carbon treatment, ozone treatment or

ultraviolet irradiation treatment, or any combination of two or more of these treatments, may be performed as required.

[0120]

In the water treatment apparatus 3, in addition to the reverse osmosis membranes, the system may also include a pump, safety filter, flow rate measurement device, pressure measurement device, temperature measurement device, oxidation-reduction potential (ORP) measurement device, residual chlorine measurement device, electrical conductivity measurement device, pH measurement device, and/or energy recovery device or the like as required.

[0121]

In the water treatment system 5, if necessary, pH adjusters and scale inhibitors other than the stabilized hypobromous acid composition or stabilized hypochlorous acid composition may be added to at least one of the biologically treated water, the membrane treated water and the ammonia-reduced water in at least one location among the biologically treated water tank 52 and the lines either side thereof, the membrane treated water tank 58 and the lines either side thereof, and the ammonia-reduced water tank 32 and the lines either side thereof.

[0122]

<Antimicrobial Agent>

The antimicrobial agent according to an embodiment of the present invention 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.

[0123]

Further, the antimicrobial agent according to another embodiment of the present invention 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.

[0124]

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

[0125]

Examples of commercially available stabilized hypochlorous acid compositions containing a chlorine-based oxidizing agent and a sulfamic acid compound include the product "Kuriverter IK-110" manufactured by Kurita Water Industries Ltd.

10 [0126]

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
15 water, or alternatively, contains a reaction product of bromine and a sulfamic acid compound, for example, a mixture of a reaction product of bromine and a sulfamic acid compound, an alkali and water.

[0127]

20 Compared with antimicrobial agents containing a chlorine-based oxidizing agent and a sulfamic acid compound (such as chlorosulfamic acid), of the various antimicrobial agents according to embodiments of the present invention, antimicrobial agents containing a stabilized hypobromous acid composition containing a bromine-based oxidizing agent and a sulfamic acid compound, and particularly antimicrobial agents containing a stabilized hypobromous acid composition containing bromine and a sulfamic acid compound, can
25 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 compositions of similarly high oxidizing power such as hypochlorous acid. At general

usage concentrations, the effects on membrane degradation can be essentially ignored. As a result, these agents are ideal as antimicrobial agents.

[0128]

5 Unlike hypochlorous acid, the antimicrobial agents according to embodiments of the present invention undergo almost no permeation through the reverse osmosis membrane, and therefore may 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.

[0129]

10 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.

[0130]

The bromate concentration in the antimicrobial agent is preferably less than 5 mg/kg.
15 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.

[0131]

<Method for Producing Antimicrobial Agent>

The antimicrobial agent according to an embodiment of the present invention is
20 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.

[0132]

The method for producing an antimicrobial agent that contains a stabilized hypobromous acid composition containing bromine and a sulfamic acid compound
25 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 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.

[0133]

5 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.

[0134]

10 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.

[0135]

15 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
20 effect may be inferior.

[0136]

25 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.

EXAMPLES

[0137]

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

[0138]

[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.

[0139]

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.

[0140]

5 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
10 (9.18) of a borate standard solution (type 2) manufactured by the same company.

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.

15 [0141]

[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
20 was 13.7, and the total chlorine concentration was 6.2 wt%.

[0142]

[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

25 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.

[0143]

(Mori-Okamoto equation)

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

Here,

z: distance from cell center position

5 $U_{\text{obs}}(z)$: 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

10 U_0 : average mobility on upper and lower surfaces of cell

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

(Smoluchowski equation)

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

Here,

15 U: electric mobility

ε : dielectric constant of solvent

η : viscosity of solvent

[0144]

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.

25 [0145]

[Test Conditions and Test Method]

The permeation rate of antimicrobial agents was measured by a flat membrane test.

A Membrane Master C70 - F flow-type flat membrane test cell manufactured by Nitto

Denko Corporation was used for the flat membrane cell. Reverse osmosis membranes ES15, ES10C and LFC3 manufactured by Nitto Denko Corporation, a reverse osmosis membrane OFR625 manufactured by Organo Corporation, and a reverse osmosis membrane TML20 manufactured by Toray Industries, Inc. were used as the flat membranes. LFC3 manufactured by Nitto Denko Corporation is a representative neutral membrane. ES10C manufactured by Nitto Denko Corporation is a membrane marketed as a cationically charged membrane. TML20 manufactured by Toray Industries, Inc., and OFR625 manufactured by Organo Corporation are neutral membranes, whereas ES15 manufactured by Nitto Denko Corporation is an anionically charged membrane. The flat membranes that were used were circular, with a diameter of 75 mm. The flow is illustrated in FIG. 2.

[0146]

For the test water (the water to be treated) for the flat membrane test, a solution prepared by adding the antimicrobial agent to a solution prepared by dissolving 500 mg/L of sodium chloride in pure water, and then using hydrochloric acid or sodium hydroxide to adjust the pH to 7.0 was used. The antimicrobial agent was added so as to achieve a concentration of the antimicrobial agent equivalent to a total chlorine concentration of about 3 to 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 membranes 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, and the antimicrobial agent permeation rate was determined. 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).

[0147]

Ammonium chloride was added to achieve an ammonia concentration of 0 mg/L, 1 mg/L, 5 mg/L or 10 mg/L, the concentration of each antimicrobial agent in the water to be

treated (total chlorine concentration) and the permeate (total chlorine concentration) were measured, and the permeation rate was calculated. The measurement results are shown in Table 1.

[0148]

[Table 1]

Membrane type	Zeta potential (charge type)	Ammonium ion concentration	Raw water Antimicrobial agent concentration	Permeate Antimicrobial agent concentration	Antimicrobial agent permeation rate
	mV	mg/L	mg/L	mg/L	%
LFC3	-1.3 (neutral)	0	10.7	0.01	0.1
		1	9.8	0.05	0.5
		5	9.6	0.11	1.1
		10	7.4	0.38	5.1
TML20	-3.9 (neutral)	0	9.9	0.06	0.6
		1	7.0	0.25	3.6
		5	7.6	0.54	7.1
		10	5.5	0.45	8.2
OFR625	-9.6 (neutral)	0	10.5	0.05	0.5
		1	6.8	0.17	3.7
		5	3.6	0.36	10.0
		10	4.7	0.52	11.1
ES10C	5~20 (cationic)	0	10.5	0.02	0.2
		1	8.3	0.06	0.7
		5	6.7	0.33	5.0
		10	6.2	0.35	5.7
ES15	-35 (anionic)	0	11.5	0.07	0.6
		1	5.3	0.33	6.2
		5	4.2	0.68	16.2
		10	3.3	0.59	17.9

5 [0149]

<Example 1>

In Example 1, the stabilized hypobromous acid composition (the composition 1) was used as the antimicrobial agent, and the antimicrobial agent permeation rate (%) was measured at each of the zeta potential values (mV) when the ammonium ion concentration was 10 mg/L (Example 1-1), 5 mg/L (Example 1-2) or 1 mg/L (Example 1-3). The results are shown in FIG. 3.

[0150]

<Comparative Example 1>

In Comparative Example 1, the stabilized hypobromous acid composition (the composition 1) was used as the antimicrobial agent, and the antimicrobial agent permeation rate (%) was measured at each of the zeta potential values (mV) when the ammonium ion concentration was 0 mg/L (Comparative Example 1-1). The results are shown in FIG. 3.

5 [0151]

In Comparative Example 1, the permeation rate of the antimicrobial agent was low, and almost no dependency of the permeation rate on the zeta potential was observed, whereas in Example 1, the antimicrobial agent permeation rate was higher, and moreover, a tendency for a lower permeation rate at higher zeta potential values was observed. This
10 tendency was particularly noticeable when the ammonium ion concentration was 5 mg/L or higher.

[0152]

<Example 2>

In Example 2, the stabilized hypobromous acid composition (the composition 1) was
15 used as the antimicrobial agent, and the antimicrobial agent permeation rate was measured for neutral membranes (OFR625 (Example 2-1), TML20 (Example 2-2) and LFC3 (Example 2-4)) and a cationically charged membrane (ES10C (Example 2-3)). The correlations between the antimicrobial agent permeation rate (%) and the ammonium ion concentration (mg/L) are shown in FIG. 4.

20 [0153]

<Comparative Example 2>

In Comparative Example 2, the stabilized hypobromous acid composition (the composition 1) was used as the antimicrobial agent, and the antimicrobial agent permeation rate was measured for an anionically charged membrane (ES15 (Comparative Example 2-1)).
25 The correlation between the antimicrobial agent permeation rate (%) and the ammonium ion concentration (mg/L) is shown in FIG. 4.

[0154]

The antimicrobial agent permeation rate decreased more in Example 2 than in Comparative Example 2. In particular, the difference in the permeation rates was larger when the ammonium ion concentration was 5 mg/L or higher.

[0155]

5 <Example 3>

In Example 3, the antimicrobial agent was changed to the stabilized hypochlorous acid composition (the composition 2), and the permeation rate was measured for a neutral membrane (LFC3 (Example 3-1)) in the same manner as Example 2. The correlation between the antimicrobial agent permeation rate (%) and the ammonium ion concentration (mg/L) is shown in FIG. 5.

[0156]

<Comparative Example 3>

In Comparative Example 3, the antimicrobial agent was changed to the stabilized hypochlorous acid composition (the composition 2), and the permeation rate was measured for an anionically charged membrane (ES15 (Comparative Example 3-1)) in the same manner as Comparative Example 2. The correlation between the antimicrobial agent permeation rate (%) and the ammonium ion concentration (mg/L) is shown in FIG. 5.

[0157]

Even in the case of a chlorine-based stabilized hypochlorous acid composition, the permeation rate for the antimicrobial agent was lower when a neutral membrane or cationically charged membrane was used. Moreover, the difference in the permeation rates was larger when the ammonium ion concentration was 5 mg/L or higher.

[0158]

As outlined above, by using the method described in the examples in a water treatment method used for treating, with a reverse osmosis membrane, a water to be treated containing ammonia, permeation through the reverse osmosis membrane of an antimicrobial agent containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound was able to be suppressed.

[0159]

<Example 4, Comparative Example 4>

[Test Conditions and Test Method]

The permeation rate of antimicrobial agents was measured by a flat membrane test.

5 A Membrane Master C70 - F flow-type flat membrane test cell manufactured by Nitto Denko Corporation was used for the flat membrane cell. Reverse osmosis membranes ES15 (Comparative Example 4) and LFC3 (Example 4) manufactured by Nitto Denko Corporation were used as the flat membranes. ES15 manufactured by Nitto Denko Corporation is an anionically charged membrane (zeta potential: -35 mV), whereas LFC3
10 manufactured by Nitto Denko Corporation is a neutral membrane (zeta potential: -1.3 mV). The flat membranes that were used were circular, with a diameter of 75 mm. The flow is illustrated in FIG. 2.

[0160]

For the test water (the water to be treated) for the flat membrane test, a solution
15 prepared by adding the antimicrobial agent (the composition 1 (Example 4-1 and Comparative Example 4-1) or the composition 2 (Example 4-2 and Comparative Example 4-2)) to a solution prepared by dissolving 500 mg/L of sodium chloride in pure water, and then using hydrochloric acid or sodium hydroxide to adjust the pH to 7.0 was used. The antimicrobial agent was added so as to achieve a concentration of the antimicrobial agent
20 equivalent to a total chlorine concentration of about 3 to 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 membranes was set to 0.75 MPa. The feed water was supplied to the reverse osmosis membrane at 5 L/min.

[0161]

25 Ammonium chloride was added to achieve an ammonia concentration of 0 mg/L, 1 mg/L, 5 mg/L or 10 mg/L, and after supplying the water to the reverse osmosis membrane for about 3 hours, the concentration of each antimicrobial agent in the water to be treated (total chlorine concentration) and the permeate (total chlorine concentration) were measured,

and the permeation rate was calculated. The measurement results are shown in Table 2, and the correlations between the antimicrobial agent permeation rate (%) and the ammonium ion concentration (mg/L) are shown in FIG. 8 (for the composition 1 (Example 4-1 and Comparative Example 4-1)) and FIG. 9 (for the composition 2 (Example 4-2 and Comparative Example 4-2)).

[0162]

[Table 2]

Antimicrobial agent	Membrane type	Ammonium ion concentration	Water to be treated antimicrobial agent concentration	Permeate antimicrobial agent concentration	Antimicrobial agent permeation rate
		mg/L	mg/L	mg/L	%
Hypobromous acid + sulfamic acid (composition 1)	ES15	0	11.5	0.07	0.6
		1	5.3	0.33	6.2
		5	4.2	0.68	16.2
		10	3.3	0.59	17.9
		30	3.0	0.56	18.5
	LFC3	0	10.7	0.01	0.1
		1	9.8	0.05	0.5
		5	9.6	0.11	1.1
		10	7.4	0.38	5.1
		30	6.6	0.83	12.4
Hypochlorous acid + sulfamic acid (composition 2)	ES15	0	10.8	0.09	0.8
		1	10.8	0.15	1.4
		5	10.7	0.32	3.0
		10	10.9	0.43	3.9
	LFC3	0	10.8	0.05	0.5
		1	10.8	0.08	0.7
		5	10.7	0.19	1.8
		10	10.9	0.29	2.7

[0163]

10 The antimicrobial agent permeation rate increased with increasing ammonia concentration. In particular, when the ammonia concentration was 5 mg/L or higher, the tendency for the permeation rate to increase was comparatively large, and it is considered

that performing a pretreatment to reduce the ammonia concentration to not more than 5 mg/L is desirable.

[0164]

Further, in terms of the types of reverse osmosis membranes used in the present system, it was evident that use of the neutral membrane LFC3 yielded a lower antimicrobial agent permeation rate than the anionically charged membrane ES15.

[0165]

<Examples 5 to 8 and Comparative Examples 5 and 6>

Testing was conducted using a pilot apparatus illustrated in FIG. 10. For the raw water (the water to be treated), a solution prepared by dissolving 500 mg/L of sodium chloride in pure water and then adjusting the pH to 7.0 was used. Hydrochloric acid or sodium hydroxide was used as the pH adjuster. Either LFC3 (Examples 5 to 8) or ES15 (Comparative Examples 5 and 6), both manufactured by Nitto Denko Corporation, was used as the reverse osmosis membrane, the water treatment rate for the raw water was set to 25 m³/d, the temperature of the feed water was set to 25°C, and the supply pressure was set to 0.75 MPa. The stabilized hypobromous acid composition (the composition 1) was used as the antimicrobial agent, and the total chlorine concentration was measured as the concentration of the antimicrobial agent.

[0166]

(Examples 5 and 6, Comparative Example 5)

In Example 5 and Comparative Example 5-1, an ammonia stripping device was used as an ammonia reduction unit, whereas in Example 6 and Comparative Example 5-2, the ammonia stripping device was not used. Ammonium chloride was added to the raw water (the water to be treated) in an amount sufficient to generate an ammonia concentration of 200 mg/L, 100 mg/L or 20 mg/L. The liquid temperature at which the ammonia stripping was performed was set to 80°C, and the pH was set to 10. At this time, the ammonia concentration of the water to be treated and the water at the reverse osmosis membrane inlet, and the antimicrobial agent concentration (total chlorine) of the water at the reverse osmosis

membrane inlet and the treated water were measured, and the antimicrobial agent permeation rate was calculated for each set of conditions. The results are shown in Table 3.

[0167]

[Table 3]

	RO membrane type	Water to be treated ammonia concentration [mg/L]	RO inlet ammonia concentration [mg/L]	RO inlet antimicrobial agent concentration (total chlorine) [mg/L]	Treated water antimicrobial agent concentration (total chlorine) [mg/L]	Antimicrobial agent permeation rate [%]	Antimicrobial agent permeation rate ratio
Example 5-1	LFC3	200	11	9.3	0.5	5.1	0.268 times (Example 5/ Example 6)
Example 6-1			199	8.9	1.7	19	
Example 5-2	LFC3	100	5.0	9.8	0.1	1.1	0.069 times (Example 5/ Example 6)
Example 6-2			98	9.4	1.5	16	
Example 5-3	LFC3	20	1.1	10.8	0.1	0.5	0.058 times (Example 5/ Example 6)
Example 6-3			19	10.2	0.9	8.6	
Comparative Example 5-1	ES15	20	1.1	10.8	0.8	7	0.389 times (Comparative Example 5-1/ Comparative Example 5-2)
Comparative Example 5-2			19	10.2	1.8	18	

[0168]

In Example 5, the antimicrobial agent permeation rate was able to be reduced compared with Example 6. Further, when the ammonia concentration of the water to be treated was 100 mg/L or less, the ammonia concentration at the reverse osmosis membrane inlet was not more 5 mg/L, and the antimicrobial agent permeation rate was 0.069 times or less that of Example 6, indicating that the permeation rate was able to be reduced particularly effectively.

[0169]

(Examples 7 and 8, Comparative Example 6)

10 In Example 7 and Comparative Example 6-1, an oxidizing agent was added as a means for reducing the ammonia, whereas in Example 8 and Comparative Example 6-2, the oxidizing agent was not added. The stabilized hypobromous acid composition (the composition 1) added at the latter-stage reverse osmosis membrane was added as the oxidizing agent. Ammonium chloride was added to the raw water (the water to be treated)

15 in an amount sufficient to generate an ammonia concentration of 20 mg/L, 15 mg/L or 3 mg/L. The concentration of the added oxidizing agent, expressed as total chlorine, was set to 10 mg/L, and the pH was set to 7.2. The oxidative decomposition reaction time was set to 30 minutes. The results are shown in Table 4.

[0170]

[Table 4]

	RO membrane type	Water to be treated ammonia concentration [mg/L]	RO inlet ammonia concentration [mg/L]	RO inlet antimicrobial agent concentration (total chlorine) [mg/L]	Treated water antimicrobial agent concentration (total chlorine) [mg/L]	Antimicrobial agent permeation rate [%]	Antimicrobial agent permeation rate ratio
Example 7-1	LFC3	20	6.4	10.8	0.2	2.3	0.267 times (Example 7/ Example 8)
Example 8-1			20	10.2	0.9	8.6	
Example 7-2	LFC3	15	4.8	10.8	0.1	1.0	0.056 times (Example 7/ Example 8)
Example 8-2			15	10.3	1.9	18	
Example 7-3	LFC3	3	1.0	10.8	0.1	0.5	0.029 times (Example 7/ Example 8)
Example 8-3			8	10.5	1.8	17	
Comparative Example 5-1	ES15	3	1.0	10.8	0.8	7	0.412 times (Comparative Example 6-1/ Comparative Example 6-2)
Comparative Example 5-2			8	10.5	1.8	17	

[0171]

In Example 7, the antimicrobial agent permeation rate was able to be reduced compared with Example 8. Further, when the ammonia concentration of the water to be treated was 15 mg/L or less, the ammonia concentration at the reverse osmosis membrane inlet was not more 5 mg/L, and the antimicrobial agent permeation rate was 0.056 times or less that of Example 8, indicating that the permeation rate was able to be reduced particularly effectively.

[0172]

<Examples 9-1 to 9-5>

A simulated wastewater was prepared from Sagami-hara City water from which residual chlorine had been removed with activated carbon, by dissolving ammonium chloride in the water in an amount sufficient to prepare an aqueous solution having an ammoniacal nitrogen ($\text{NH}_4\text{-N}$) concentration of 7.8 mg-N/L (0.56 mmol/L). The pH of the thus prepared simulated wastewater was 7.2. The stabilized hypobromous acid composition (the composition 1) (Examples 9-1 to 9-5) was added to the prepared simulated wastewater in an amount sufficient to obtain an effective halogen concentration of 15 mg/L as Cl_2 (0.21 mmol/L) (Example 9-1), 40 mg/L as Cl_2 (0.56 mmol/L) (Example 9-2), 61 mg/L as Cl_2 (0.87 mmol/L) (Example 9-3), 79 mg/L as Cl_2 (1.11 mmol/L) (Example 9-4) or 99 mg/L as Cl_2 (1.40 mmol/L) (Example 9-5). The change in the concentration of ammoniacal nitrogen ($\text{NH}_4\text{-N}$) over time (after 10 minutes and after 30 minutes) was measured while the test liquid was stirred at 500 rpm using a digital stirrer. After 30 minutes, the total chlorine concentration of the test water was measured. The results are shown in Table 5.

[0173]

The total chlorine concentration represents the value (mg/L as Cl_2) measured by the total chlorine measurement method (DPD (diethyl-p-phenylenediamine) method) using a multipurpose water quality analyzer DR/4000 manufactured by Hach Company. The ammoniacal nitrogen ($\text{NH}_4\text{-N}$) concentration (mg/L as N) was measured using the coloration principle of the indophenol blue absorptiometry method of JIS K 0102 42.2, using a

PACKTEST (ammonium nitrogen, model: WAK-NH₄) from Kyoritsu Chemical-Check Lab., Corp.

[0174]

5 In Table 5, it was evident that the reduction effect on ammoniacal nitrogen increased as the ratio of the effective halogen molar concentration (the added molar concentration of the stabilized hypobromous acid composition) calculated as a total chlorine concentration relative to the molar concentration (0.56 mmol/L) of ammoniacal nitrogen (NH₄-N) in the simulated wastewater prior to treatment increased. In particular, it was evident that when the ratio of the effective halogen molar concentration (the added molar concentration of the
10 stabilized hypobromous acid composition) calculated as a total chlorine concentration relative to the molar concentration of ammoniacal nitrogen (NH₄-N) in the simulated wastewater was 1.6 (Example 9-3) or greater, the ammoniacal nitrogen was able to be substantially completely decomposed.

[0175]

[Table 5]

		Example 9-1	Example 9-2	Example 9-3	Example 9-4	Example 9-5
Added reagent		Stabilized hypobromous acid composition (composition 1)				
Added reagent concentration	[mg/L as Cl ₂]	15	40	61	79	99
	[mmol/L as Cl ₂]	0.21	0.56	0.87	1.11	1.40
NH ₄ -N concentration in simulated wastewater	[mg/L]	7.8				
	[mmol/L]	0.56				
Ratio of added reagent molar concentration relative to NH ₄ -N molar concentration in simulated wastewater		0.4	1.0	1.6	2.0	2.5
NH ₄ -N concentration in simulated wastewater [mg/L]	before treatment	7.8	7.8	7.8	7.8	7.8
	after 10 minutes	2.9	2.3	0.9	0	0
	after 30 minutes	2.5	2.2	0.8	0	0
Total chlorine concentration in simulated wastewater [mg/L as Cl ₂]	after 30 minutes	3.9	4.4	4.5	14.5	32.0

[0176]

As described above, by using the method described in the examples in a water treatment method used for treating, with a reverse osmosis membrane, a water to be treated containing ammonia, permeation through the reverse osmosis membrane of an antimicrobial agent containing a chlorine-based oxidizing agent or a bromine-based oxidizing agent and a sulfamic acid compound was able to be suppressed.

REFERENCE SIGNS LIST

[0177]

- 10 1, 5: Water treatment system
- 3: Water treatment apparatus
- 10, 50: Biological treatment device
- 12, 52: Biologically treated water tank
- 14, 54: Membrane treatment device
- 15 16, 56: Biological treatment system
- 18, 58: Membrane treated water tank
- 20: Treatment water tank
- 22, 34: Reverse osmosis membrane treatment device
- 24, 60: Second reverse osmosis membrane treatment device
- 20 26: Reverse osmosis membrane treatment system
- 30: Ammonia reduction device
- 32: Ammonia-reduced water tank
- 36: Water to be treated line
- 38: Ammonia-reduced water line
- 25 40: Antimicrobial agent-containing water line
- 42: Permeate line
- 44: Concentrate line
- 46: Antimicrobial agent addition line

CLAIMS

1. A water treatment method using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, 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,
the reverse osmosis membrane is a neutral membrane or a cationically charged membrane, and
an amount of ammonia in the water to be treated containing ammonia is reduced, and the antimicrobial agent is then introduced into an ammonia-reduced water in which the amount of ammonia has been reduced.
2. A water treatment method using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, wherein
an antimicrobial agent comprising bromine and a sulfamic acid compound is introduced into the water to be treated,
the reverse osmosis membrane is a neutral membrane or a cationically charged membrane, and
an amount of ammonia in the water to be treated containing ammonia is reduced, and the antimicrobial agent is then introduced into an ammonia-reduced water in which the amount of ammonia has been reduced.
3. The water treatment method using a reverse osmosis membrane according to Claim 1 or 2, wherein
an ammonium ion concentration in the water to be treated is at least 1 mg/L.
4. The water treatment method using a reverse osmosis membrane according to any one of Claim 1 to 3, wherein an ammonia concentration of the ammonia-reduced water is not more than 5 mg/L.
5. The water treatment method using a reverse osmosis membrane according to any one of Claim 1 to 4, wherein ammonia in the water to be treated containing ammonia is reduced by an ammonia stripping treatment.

6. The water treatment method using a reverse osmosis membrane according to any one of Claim 1 to 4, wherein ammonia in the water to be treated containing ammonia is reduced by an ammonia decomposition treatment using an oxidizing agent.
7. A water treatment apparatus using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, wherein the water treatment apparatus comprises:
- an ammonia reduction unit that reduces an amount of ammonia in the water to be treated containing ammonia to obtain an ammonia-reduced water;
 - a supply of an antimicrobial agent arranged to introduce the antimicrobial agent into the water to be treated containing ammonia and the ammonia-reduced water, wherein
 - the antimicrobial agent comprises a bromine-based oxidizing agent or a chlorine-based oxidizing agent and a sulfamic acid compound; and
 - wherein the reverse osmosis membrane is a neutral membrane or a cationically charged membrane.
8. A water treatment apparatus using a reverse osmosis membrane for treating, with the reverse osmosis membrane, a water to be treated containing ammonia, wherein the water treatment apparatus comprises:
- an ammonia reduction unit that reduces an amount of ammonia in the water to be treated containing ammonia to obtain an ammonia-reduced water;
 - a supply of an antimicrobial agent arranged to introduce the antimicrobial agent into the water to be treated containing ammonia and the ammonia-reduced water, wherein
 - the antimicrobial agent comprises bromine and a sulfamic acid compound; and
 - wherein the reverse osmosis membrane is a neutral membrane or a cationically charged membrane.
9. The water treatment apparatus using a reverse osmosis membrane according to Claim 7 or 8, wherein an ammonium ion concentration in the water to be treated is at least 1 mg/L.

10. The water treatment apparatus using a reverse osmosis membrane according to any one of Claim 7 to 9,
wherein
an ammonia concentration of the ammonia-reduced water is not more than 5 mg/L.
11. The water treatment apparatus using a reverse osmosis membrane according to any one of Claim 7 to 10,
comprising an ammonia stripping treatment device as the ammonia reduction unit.
12. The water treatment apparatus using a reverse osmosis membrane according to any one of Claim 7 to 10,
comprising an ammonia decomposition treatment unit using an oxidizing agent as the ammonia
reduction unit.