

DESCRIPTION

WATER TREATMENT SYSTEM AND WATER TREATMENT METHOD USING REVERSE OSMOSIS MEMBRANE

5

TECHNICAL FIELD

[0001]

The present invention relates to a water treatment system and water treatment method using a reverse osmosis membrane.

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BACKGROUND

[0002]

In water treatment using reverse osmosis membranes (RO membranes), the formation of slime is frequently a problem, and this is currently controlled by addition of an organic antimicrobial agent, or by addition of a chlorine-based antimicrobial agent and a bromine-based antimicrobial agent (for example, see Patent Document 1 and Patent Document 2). In order to improve the treated water quality from reverse osmosis membranes, it is desirable for reverse osmosis membranes to have a high rejection rate with respect to such antimicrobial agents.

20 [0003]

Furthermore, as disclosed in Patent Document 3, water treatment can be performed using two stages of reverse osmosis membranes. In the method of Patent Document 3, because most of the antimicrobial agent is rejected at the first stage reverse osmosis membrane, slime control at the second stage reverse osmosis membrane requires further addition of antimicrobial agent, and a chlorine-based antimicrobial agent is typically applied at the first stage reverse osmosis membrane, while an alkali antimicrobial agent is applied at the second stage reverse osmosis membrane. However, because injection

points are required at two locations, and the amount of antimicrobial agent added also tends to increase, the device becomes complex and operation costs also rise.

CITATION LIST

5 PATENT LITERATURE

[0004]

Patent Document 1: JP 2006-263510 A

Patent Document 2: JP 2015-062889 A

Patent Document 3: JP 5050605 B

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SUMMARY

TECHNICAL PROBLEM

[0005]

15 An object of the present invention is to provide a water treatment system and a water treatment method that are capable of reducing the amount of antimicrobial agent added in a water treatment using two or more stages of reverse osmosis membranes.

SOLUTION TO PROBLEM

[0006]

20 The present invention provides a water treatment system using two or more stages of reverse osmosis membranes, the water treatment system including at least a first stage reverse osmosis membrane device, a second stage reverse osmosis membrane device for treating a permeate of the first stage reverse osmosis membrane device, and a circulation mechanism for circulating a concentrate of the second stage reverse osmosis membrane device to a supply water of the first stage reverse osmosis membrane device, wherein an
25 antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is added to a supply water of the second stage reverse osmosis membrane.

[0007]

In the above water treatment system, the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is preferably at least one of a hypobromous acid stabilized composition, chlorosulfamic acid, hypochlorous acid, hypobromous acid, an isothiazolone compound, and a halocyanoacetamide compound.

5 [0008]

In the above water treatment system, a degassing membrane for degassing the supply water of the second stage reverse osmosis membrane is preferably provided at a stage subsequent to addition of the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70%.

10 [0009]

In the above water treatment system, the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is preferably an anionic antimicrobial agent, and the second stage reverse osmosis membrane device preferably contains an anionically-charged membrane.

15 [0010]

In the above water treatment system, the first stage reverse osmosis membrane device preferably contains a neutral membrane.

[0011]

Furthermore, the present invention provides a water treatment method for
20 performing two or more stages of reverse osmosis membrane treatment using at least a first stage reverse osmosis membrane, and a second stage reverse osmosis membrane for treating a permeate of the first stage reverse osmosis membrane, the method including using a concentrate of the second stage reverse osmosis membrane by circulating the concentrate to a supply water of the first stage reverse osmosis membrane, and adding an
25 antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% to a supply water of the second stage reverse osmosis membrane.

[0012]

In the above water treatment method, the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is preferably at least one of a hypobromous acid stabilized composition, chlorosulfamic acid, hypochlorous acid, hypobromous acid, an isothiazolone compound, and a halocyanoacetamide compound.

5 [0013]

In the above water treatment method, the supply water of the second stage reverse osmosis membrane is preferably degassed using a degassing membrane at a stage subsequent to the addition of the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70%.

10 [0014]

In the above water treatment method, the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is preferably an anionic antimicrobial agent, and the second stage reverse osmosis membrane is preferably an anionically-charged membrane.

15 [0015]

In the above water treatment method, the first stage reverse osmosis membrane is preferably a neutral membrane.

ADVANTAGEOUS EFFECTS OF INVENTION

20 [0016]

The present invention is able to provide water treatment system and a water treatment method that are capable of reducing the amount of antimicrobial agent added in a water treatment using two or more stages of reverse osmosis membranes.

25 BRIEF DESCRIPTION OF DRAWINGS

[0017]

FIG. 1 is a schematic structural diagram illustrating one example of a water treatment system according to an embodiment of the present invention.

FIG. 2 is a schematic structural diagram illustrating another example of a water treatment system according to an embodiment of the present invention.

FIG. 3 is a schematic structural diagram illustrating a conventional water treatment system.

5 FIG. 4 is a schematic structural diagram of a flat membrane testing apparatus used for evaluating the rejection rate of the reverse osmosis membrane in the Examples.

DESCRIPTION OF EMBODIMENTS

[0018]

10 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.

[0019]

<Water Treatment System and Water Treatment Method>

15 A schematic of an example of the water treatment system according to an embodiment of the present invention is illustrated in FIG. 1, and the structure of that system is described below. The water treatment system 1 includes a first stage first reverse osmosis membrane device 12, and a second stage second reverse osmosis membrane device 14. The water treatment system 1 may include a raw water tank 10 at a
20 stage prior to the first reverse osmosis membrane device 12.

[0020]

In the water treatment system 1 of FIG. 1, a line 16 is connected to the raw water inlet of the raw water tank 10, and the outlet of the raw water tank 10 and the inlet of the first reverse osmosis membrane device 12 are connected by a line 18. The permeate
25 outlet of the first reverse osmosis membrane device 12 and the inlet of the second reverse osmosis membrane device 14 are connected by a line 20, and a line 24 is connected to the permeate outlet of the second reverse osmosis membrane device 14. A line 22 is connected to the concentrate outlet of the first reverse osmosis membrane device 12, and

the concentrate outlet of the second reverse osmosis membrane device 14 and the concentrate inlet of the raw water tank 10 are connected by a circulation line 26 that functions as a circulation mechanism. An antimicrobial agent addition line 28 that functions as an antimicrobial agent addition mechanism is connected to the line 20.

5 [0021]

The water treatment method and the operation of the water treatment system 1 according to the present embodiment are described below.

[0022]

The raw water that represents the treatment target may be stored in the raw water
10 tank 10 through the line 16 as required, and is then fed through the line 18 to the first stage first reverse osmosis membrane device 12. In the first reverse osmosis membrane device 12, the first stage of a reverse osmosis membrane treatment is performed (first reverse osmosis membrane treatment step). The first permeate from the first reverse osmosis membrane device 12 is fed through the line 20 to the second stage second reverse osmosis
15 membrane device 14, and the first concentrate is discharged through the line 22.

[0023]

Here, at a stage prior to the second stage second reverse osmosis membrane device 14, an antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is added to the supply water of the second reverse osmosis membrane device 14,
20 for example, through the antimicrobial agent addition line 28 in the line 20 (antimicrobial agent addition step). Although the antimicrobial agent may or may not be added to the supply water of the first stage first reverse osmosis membrane device 12, the antimicrobial agent is preferably not added. The amount of antimicrobial agent added can be further reduced by not adding the antimicrobial agent to the supply water of the first stage first
25 reverse osmosis membrane device 12.

[0024]

In the second reverse osmosis membrane device 14, a second stage reverse osmosis membrane treatment is performed (second reverse osmosis membrane treatment step).

The second permeate from the second reverse osmosis membrane device 14 is discharged through the line 24 as treated water, and the second concentrate is circulated through the circulation line 26 to the supply water of the first stage first reverse osmosis membrane device 12, for example, to the raw water tank 10 (circulation step). In the circulation step, the second concentrate may be circulated back into the line 16, the line 18, or the like.

[0025]

Since the antimicrobial agent added to the supply water of the second reverse osmosis membrane device 14 is an antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70%, most of the antimicrobial agent can be rejected by the second stage reverse osmosis membrane and can be retained on the second concentrate side. In the flow that circulates the second concentrate of the second stage second reverse osmosis membrane device 14 to a stage prior to the first stage first reverse osmosis membrane device 12, the antimicrobial agent originating from the second concentrate of the second reverse osmosis membrane device 14 will become mixed with the supply water of the first reverse osmosis membrane device 12 (the raw water). As a result, the amount of antimicrobial agent added can be reduced in a water treatment using two or more stages of reverse osmosis membranes.

[0026]

Although two stages of reverse osmosis membranes are used in the example of FIG. 1, the system is not limited to this configuration. In the water treatment method and water treatment system using two or more stages of reverse osmosis membranes, the concentrate of the second stage reverse osmosis membrane is used by circulating the concentrate to the supply water of the first stage reverse osmosis membrane, and the amount of antimicrobial agent added can be reduced by adding the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% to the supply water of the second stage reverse osmosis membrane.

[0027]

Isothiazolone compounds, which are representative organic antimicrobial agents, permeate reverse osmosis membranes at a rate of approximately 20%, and the amount circulated to a stage prior to the first reverse osmosis membrane device 12 is reduced even in a flow in which the second concentrate of the second reverse osmosis membrane device 14 is circulated to a stage prior to the first reverse osmosis membrane device 12. Therefore, it is more preferable to use an antimicrobial agent in which at least 90%, or preferably at least 99%, is rejected by the reverse osmosis membrane.

[0028]

Since a large amount of the antimicrobial agent component is preferably circulated at the second reverse osmosis membrane device 14 directly after addition of the antimicrobial agent, it is better to employ an anionic reverse osmosis membrane (anionically-charged membrane) having a high rejection rate of the antimicrobial agent. On the other hand, if the first reverse osmosis membrane device 12 upstream from the point of addition of the antimicrobial agent is a neutral membrane having a rejection rate of the antimicrobial agent that is comparatively low, the antimicrobial agent component will be retained in subsequently stages, and therefore the amount of antimicrobial agent injected at a subsequent stage can be further reduced.

[0029]

As shown in FIG. 2, when a unit operation (for example, a degassing membrane 30 for degassing carbon dioxide gas or the like) in which biological contamination is a concern also exists between the first stage first reverse osmosis membrane device 12 and the second stage second reverse osmosis membrane device 14, biological contamination of the unit operation can be inhibited by adding the antimicrobial agent between the first stage first reverse osmosis membrane device 12 and the degassing membrane 30 and the like. In other words, by including a degassing membrane 30, or the like, that performs degassing of the supply water of the second stage second reverse osmosis membrane device 14 at a stage subsequent to addition of the antimicrobial agent having a rejection

rate by a reverse osmosis membrane of at least 70%, biological contamination of the degassing membrane 30 or the like can be inhibited.

[0030]

The reverse osmosis membrane used for the first reverse osmosis membrane device 5 12 and the second reverse osmosis membrane device 14 primarily uses a polyamide-based polymer membrane, for which neutral membranes, anionically-charged membranes, and cationically-charged membranes exist. A neutral membrane refers to a membrane having a zeta potential at pH 7.0, measured by a zeta potential measurement method described in the examples below, that is in a range of -15 to 5 (mV), while an anionically-charged 10 membrane refers to a membrane having a zeta potential at pH 7.0 of less than -15 (mV). A cellulose acetate-based polymer membrane may be used for the reverse osmosis membrane of the first reverse osmosis membrane device 12, and a polyamide-based polymer membrane may be used for the reverse osmosis membrane of the second reverse osmosis membrane device 14. In this case, an antimicrobial agent such as hypochlorous 15 acid may be added to the supply water of the first stage first reverse osmosis membrane device 12, and an antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% may be added to the supply water of the second reverse osmosis membrane device 14.

[0031]

20 Examples of commercially available neutral membranes include OFR-625 (manufactured by Organo Corporation), BW30XFR (manufactured by The Dow Chemical Company), LFC3 (manufactured by Nitto Denko Corporation), and TML20 (manufactured by Toray Industries, Inc.).

[0032]

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

[0033]

In the water treatment method and the water treatment system according to an embodiment of the present invention, if the first stage first reverse osmosis membrane device 12 includes a neutral membrane, the second stage second reverse osmosis membrane device 14 includes an anionically-charged membrane, and the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% is an anionic antimicrobial agent, then the anionic antimicrobial agent is more easily rejected by the second stage second reverse osmosis membrane device 14 (anionically-charged membrane), and therefore is more easily circulated to the first stage first reverse osmosis membrane device 12 (neutral membrane). Further, because the anionic antimicrobial agent readily permeates through the first stage first reverse osmosis membrane device 12 and the antimicrobial agent component will be retained in the supply water of the second stage second reverse osmosis membrane device 14, the amount of antimicrobial agent injected can be further reduced.

[0034]

Examples of the treatment target water (raw water) include electronic industry wastewater such as alcohol-containing water that contains an alcohol such as methanol, ethanol, or isopropanol. Since the risk of formation of slime is high for electronic industry wastewater, such as alcohol-containing water, the water treatment method and water treatment system according to the present embodiment can be favorably applied to a desalting step for electronic industry wastewater or the like.

[0035]

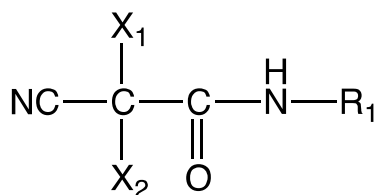
Examples of the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 70% include anionic antimicrobial agents such as a hypobromous acid stabilized composition, chlorosulfamic acid, hypochlorous acid, or hypobromous acid, and neutral antimicrobial agents such as isothiazolone compounds, including 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, and halocyanoacetamide compounds including 2,2-dibromo-3-nitrilopropionamide, while a hypobromous acid stabilized composition, chlorosulfamic acid, isothiazolone compounds,

and halocyanoacetamide compounds having a rejection rate by a reverse osmosis membrane of at least 80% are preferable, and at least one among a hypobromous acid stabilized composition, chlorosulfamic acid, and halocyanoacetamide compounds having a rejection rate by a reverse osmosis membrane of at least 90%, or specifically at least 99%, are more preferable. As described in the examples below, in this description the rejection rate by a reverse osmosis membrane refers to the rejection rate when the anionically-charged membrane “ES15” (an aromatic polyamide-based anionic membrane, manufactured by Nitto Denko Corporation) is used as the reverse osmosis membrane.

[0036]

10 The halocyanoacetamide compound is a compound represented by the general formula shown below.

[Chemical Formula 1]



(In the formula, X₁ and X₂ each independently represent a halogen atom such as F, Cl, Br or I, or a hydrogen atom, and R₁ represents a hydrogen atom or an alkyl group having a carbon number of 1 to 3.)

[0037]

<Hypobromous Acid Stabilized Composition>

The hypobromous acid stabilized composition contains a “bromine-based oxidizing agent” and a “sulfamic acid compound”, and may also further include an alkali.

[0038]

Furthermore, the hypobromous acid stabilized composition includes a “reaction product of a bromine-based oxidizing agent and a sulfamic acid compound”, and may also further include an alkali.

[0039]

The ratio of the equivalent weight of the “sulfamic acid compound” relative to the equivalent weight of the “bromine-based oxidizing agent” is preferably at least 1, and more preferably in 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” is less than 1, there is a possibility of deterioration of the reverse osmosis membrane, whereas if this ratio exceeds 2, the manufacturing costs may increase.

[0040]

Examples of the bromine-based oxidizing agent include bromine (liquid bromine), bromine chloride, bromic acid, bromate salts, and hypobromous acid. A “reaction product of a bromine compound and a chlorine-based oxidizing agent” obtained by reacting a bromine compound with a chlorine-based oxidizing agent such as a hypochlorous acid salt is also considered a “bromine-based oxidizing agent”.

[0041]

Among these, the formulation of a “bromine and sulfamic acid compound (a mixture of bromine and a sulfamic acid compound)” or a “reaction product of bromine and sulfamic acid compound” that use bromine are preferable compared to the formulation of “hypochlorous acid, a bromine compound, and sulfamic acid” and the formulation of “bromine chloride and sulfamic acid” since there are fewer chloride ions, which further prevents deterioration of the reverse osmosis membrane and lowers the possibility of causing corrosion of metallic materials, such as the lines.

[0042]

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.

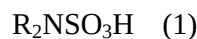
[0043]

Examples of the chlorine-based oxidizing agent include chlorine gas, chlorine dioxide, hypochlorous acid or salts thereof, chlorous acid or salts thereof, chloric acid or

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

[0044]

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



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

[0045]

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

compounds in which one of the two R groups is a hydrogen atom and the other is an aryl group having a carbon number of 6 to 10, such as N-phenylsulfamic acid, as well as salts of the above acids. Examples of the sulfamic acid salts include alkali metal salts such as sodium salts and potassium salts, alkaline earth metal salts such as calcium salts, strontium salts and barium salts, other metal salts such as manganese salts, copper salts, zinc salts, iron salts, cobalt salts and nickel salts, as well as ammonium salts and guanidine salts. One of these sulfamic acid compounds or salts may be used alone, or a combination of two or more compounds or salts may be used. In terms of the environmental burden and the like, the use of sulfamic acid (amidosulfuric acid) as the sulfamic acid compound is preferred.

[0046]

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. The alkali is typically used not as a solid, but in the form of an aqueous solution.

[0047]

The hypobromous acid stabilized composition is preferably a mixture containing bromine and a sulfamic acid compound (a composition containing a mixture of bromine and a sulfamic acid compound), such as a mixture of bromine, a sulfamic acid compound, an alkali and water, or a composition containing a reaction product of bromine and a sulfamic acid compound, such as a mixture of a reaction product of bromine and a sulfamic acid compound, an alkali and water, as such compositions may exhibit less deterioration of polyamide-based reverse osmosis membranes and the like, and suffer from less leakage of effective halogen into the RO permeate.

[0048]

The hypobromous acid stabilized composition exhibits an antimicrobial effect, and yet causes almost none of the membrane deterioration observed for hypochlorous acid and

the like. At typical usage concentrations, the effects on membrane deterioration can be substantially ignored. As a result, the composition is ideal as an antimicrobial agent.

[0049]

Unlike hypochlorous acid or the like, the hypobromous acid stabilized composition
5 can undergo almost no permeation through the reverse osmosis membrane, and therefore has almost no effect on the treated water quality. Furthermore, because the concentration can be measured on site in a similar manner to hypochlorous acid or the like, more accurate concentration control is possible.

[0050]

10 The pH of the hypobromous acid stabilized composition is, for example, higher than 13.0, and is preferably higher than 13.2. If the pH of the composition is 13.0 or lower, then the effective halogen in the composition may sometimes become unstable.

[0051]

The bromate concentration in the hypobromous acid stabilized composition is
15 preferably less than 5 mg/kg. If the bromate concentration in the hypobromous acid stabilized composition is 5 mg/kg or greater, then the concentration of bromate ions in the RO permeate and the like may increase.

[0052]

<Method for Producing Hypobromous Acid Stabilized Composition>

20 The hypobromous acid stabilized composition is obtained by mixing a bromine-based oxidizing agent and a sulfamic acid compound. An alkali may also be mixed into the composition.

[0053]

The method for producing a hypobromous acid stabilized composition that contains
25 bromine and a sulfamic acid compound, or a hypobromous acid stabilized composition that contains a reaction product of bromine and a sulfamic acid compound preferably includes a step of adding bromine, under an inert gas atmosphere, to a mixed solution containing water, an alkali and a sulfamic acid compound and inducing a reaction, 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 concentration of bromate ions in the composition can be reduced, and the bromate ion concentration in the RO permeate or the like can also be reduced.

[0054]

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.

10 [0055]

The oxygen concentration inside the reaction vessel during the bromine addition is preferably not more than 6%, more preferably not more than 4%, still more preferably not more than 2%, and most 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.

15 [0056]

The proportion of bromine added is preferably not more than 25 wt% relative to the total weight of the composition, 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 composition, then the amount of bromic acid produced in the reaction system may sometimes increase. If the proportion is less than 1 wt%, then the modifying effect may be poor.

20 [0057]

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.

5

EXAMPLES

[0058]

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

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[0059]

<Example 1 and Comparative Examples 1 and 2>

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Testing in Example 1 was performed using the water treatment system of FIG. 1, and testing in Comparative Example 1 was performed using the conventional water treatment system of FIG. 3. In the conventional water treatment system 5 of FIG. 3, an antimicrobial agent addition line 32 for addition of the antimicrobial agent to the supply water of the first stage first reverse osmosis membrane device 12 is connected to the line 18. The case where addition (injection) of the antimicrobial agent was performed at a single point from the antimicrobial agent addition line 28 (injection point 2) in the manner of FIG. 1, and the case where addition (injection) of the antimicrobial agent was performed at two points from the antimicrobial agent addition line 32 and the antimicrobial agent addition line 28 (injection point 1 and injection point 2, respectively) in the manner of FIG. 3 were compared in terms of the amount of antimicrobial agent (chemical agent) added while changing the type of antimicrobial agent according to Table 1. The concentration of the antimicrobial agent was adjusted to at least 3 mg/L before the reverse osmosis membrane. The first stage and second stage reverse osmosis membranes used the reverse osmosis membrane “ES15” manufactured by Nitto Denko Corporation, which is an anionically-charged membrane. The amount of supply water Q was 200 L/h of pure

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water, while the recovery rate of the first stage reverse osmosis membrane was 50%, and the recovery rate of the second stage reverse osmosis membrane was 90%.

[0060]

[Measurement of zeta potential of reverse osmosis membrane]

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

10 [0061]

(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

15 $U_{\text{obs}}(z)$: apparent mobility at z position in cell

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

where $K=a/b$: 2a and 2b represent horizontal and vertical lengths of cell cross-section, and $a>b$

U_p : true mobility of particle

20 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,

25 U: electric mobility

ε : dielectric constant of solvent

η : viscosity of solvent

[0062]

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 the aqueous solution and the sample were prepared, one pair was adjusted to an acidic pH (pH 2, 3, 4, 5, 6 and 7) and the other was adjusted to an alkaline pH (pH 8 and 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.

[0063]

[Evaluation of rejection rate of antimicrobial agent by reverse osmosis membrane]

For each of the antimicrobial agents of the formulation compositions shown in Table 1, the rejection rate of the antimicrobial agent by the reverse osmosis membrane was evaluated using a flat membrane test apparatus under the conditions below.

[0064]

(Test Conditions)

- Test device: flat membrane test apparatus (see FIG. 4)
- Flat membrane cell: Membrane Master C70 - F flow-type flat membrane test cell
- Flat membrane type: anionically-charged membrane “ES15” (aromatic polyamide-based anionically-charged membrane, low-pressure RO membrane, manufactured by Nitto Denko Corporation)
- Flat membrane diameter: diameter 75 mm
- Test water: ultrapure water
- Test water pH: 7.0 (as described below, adjusted with hydrochloric acid and sodium hydroxide after addition of antimicrobial agent)
- Amount of test water: 50 L
- Temperature of test water: 25°C ± 1°C
- Supply pressure: 0.75 MPa
- Amount of test water: 5 L/min
- Antimicrobial agent evaluated: see Table 1
- Antimicrobial agent concentration: 3 mg/L

[0065]

(Test Method)

Each of the antimicrobial agents was added to the test water, and after adjusting the pH, circulation was carried out for 30 min. Then, after thorough blowing of each

5 permeate, the rejection rate was calculated by sampling the raw water and the permeate, and measuring the concentration of the antimicrobial agent. The antimicrobial agent was added directly to the tank to achieve a concentration of 3 mg/L.

[0066]

The rejection rate of the reverse osmosis membrane with respect to each
10 antimicrobial agent was calculated by the following formula.

Rejection rate of reverse osmosis membrane (%) = (concentration of antimicrobial agent in supply water - concentration of antimicrobial agent in permeate) / (concentration of antimicrobial agent in supply water) × 100

[0067]

15 [Preparation of Hypobromous Acid Stabilized Composition]

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 hypobromous acid stabilized composition. The pH of the hypobromous acid stabilized composition was 14, and the effective halogen
20 concentration (effective chlorine equivalent concentration) was 7.5 wt%. A detailed description of the method for preparing the hypobromous acid stabilized composition is presented below.

[0068]

A 2 liter four-necked flask into which nitrogen gas was injected continuously at a
25 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 hypobromous acid stabilized composition containing 10.7 wt% of sulfamic acid and 16.9 wt% of bromine relative to the total weight of the composition, and having a ratio for the equivalent weight of sulfamic acid relative to the equivalent weight of bromine of 1.04. Measurement of the pH of the prepared solution using the glass electrode method yielded a value of 14. Measurement of the bromine content of the prepared solution using a method in which the bromine was substituted with iodine using potassium iodide, and a redox titration was then performed using sodium thiosulfate revealed a value of 16.9%, which was 100.0% of the theoretical content (16.9%). Further, the oxygen concentration inside the reaction vessel during the bromine reaction was measured using an "Oxygen Monitor JKO-02 LJDII" manufactured by Jikco Ltd. The bromate concentration was less than 5 mg/kg.

[0069]

[Table 1]

15

Table 1

		Example 1-1 Comparative Example 1-1	Example 1-2 Comparative Example 1-2	Example 1-3 Comparative Example 1-3	Example 1-4 Comparative Example 1-4	Comparative Example 2-1 Comparative Example 2-2	Example 2 Comparative Example 3
		Hypobromous acid stabilized composition	Isothiazolone	Hypochlorous acid	Halocyanoacetamide compound	Chloramine	Chlorosulfamic acid
Formulation composition (wt%)	Water	55	75	50		50	30
	Sodium hydroxide	13					8
	12 wt% NaClO			50		46	50
	Liquid bromine	17					
	Sulfamic acid	11					12
	Potassium hydroxide	4					
	KATHON WT		25				
	2,2-dibromo-3- nitrilopropionamide				100		
	Ammonium chloride					4	

* The concentration of the respective antimicrobial agents was adjusted to a level of 3 mg/L at the inlet of the second stage RO that performs concentrate circulation

[0070]

[Example 1-1 and Comparative Example 1-1]

In Example 1-1 and Comparative Example 1-1, the hypobromous acid stabilized composition (anionic) was added as the antimicrobial agent. At this time, measurement of the rejection rate of the hypobromous acid stabilized composition by the reverse osmosis membrane (RO rejection rate) revealed a value of 99.1%.

[0071]

In Comparative Example 1-1, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, the amount of antimicrobial agent added (X1 + X2) was 21.5 g/d. Next, in Example 1-1, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent concentration C1 in the supply water of the first reverse osmosis membrane device 12 was 3 mg/L, the amount of antimicrobial agent added X2 was 14.5 g/d, and the antimicrobial agent concentration C2 was 6.1 mg/L (> 3 mg/L). In comparison to Comparative Example 1-1, the amount of antimicrobial agent added in Example 1-1 was reduced by 7.0 g/d. The result is shown in Table 2.

[0072]

[Example 1-2 and Comparative Example 1-2]

In Example 1-2 and Comparative Example 1-2, isothiazolone (neutral) was added as the antimicrobial agent. In the formulation, KATHON (registered trademark) WT (manufactured by The Dow Chemical Company), which is an antimicrobial agent containing an isothiazolone compound, was used. At this time, measurement of the rejection rate of isothiazolone by the reverse osmosis membrane revealed a value of 81.8%.

[0073]

In Comparative Example 1-2, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the

antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, the amount of antimicrobial agent added ($X1 + X2$) was 20.3 g/d. Next, in Example 1-2, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent concentration C1 in the supply water of the first reverse osmosis membrane device 12 was 3 mg/L, the amount of antimicrobial agent added X2 was 16.1 mg/L, and the antimicrobial agent concentration C2 was 7.3 mg/L (> 3 mg/L). In comparison to Comparative Example 1-2, the amount of antimicrobial agent added in Example 1-2 was reduced by 4.2 g/d. The result is shown in Table 2.

10 [0074]

[Example 1-3 and Comparative Example 1-3]

In Example 1-3 and Comparative Example 1-3, hypochlorous acid (anionic) was added as the antimicrobial agent. At this time, measurement of the rejection rate of hypochlorous acid by the reverse osmosis membrane revealed a value of 71.0%.

15 [0075]

In Comparative Example 1-3, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, and the amount of antimicrobial agent added ($X1 + X2$) was 19.5 g/d. Next, in Example 1-3, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent concentration C1 in the supply water of the first reverse osmosis membrane device 12 was 3 mg/L, the amount of antimicrobial agent added X2 was 17.8 g/d, and the antimicrobial agent concentration C2 was 8.3 mg/L (> 3 mg/L). In comparison to Comparative Example 1-3, the amount of antimicrobial agent added in Example 1-3 was reduced by 1.7 g/d. The result is shown in Table 2.

[0076]

[Example 1-4 and Comparative Example 1-4]

In Example 1-4 and Comparative Example 1-4, a halocynoacetamide compound was used as the antimicrobial agent. At this time, measurement of the rejection rate of the halocynoacetamide compound by the reverse osmosis membrane revealed a value of 97.0%.

5 [0077]

In Comparative Example 1-4, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, the amount of antimicrobial agent added (X1 + X2) was 21.4 g/d. Next, in Example 1-4, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent concentration C1 in the supply water of the first reverse osmosis membrane device 12 was 3 mg/L, the amount of antimicrobial agent added X2 was 14.6 g/d, and the antimicrobial agent concentration C2 was 6.2 mg/L (> 3 mg/L). In comparison to Comparative Example 1-4, the amount of antimicrobial agent added in Example 1-4 was reduced by 6.8 g/d. The result is shown in Table 2.

[0078]

[Comparative Example 2-1 and Comparative Example 2-2]

In Comparative Example 2-1 and Comparative Example 2-2, chloramine (anionic) was used as the antimicrobial agent. At this time, measurement of the rejection rate of chloramine by the reverse osmosis membrane revealed a value of 10.2%.

[0079]

In Comparative Example 2-2, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, and the amount of antimicrobial agent added (X1 + X2) was 15.1 g/d. Next, in Comparative Example 2-1, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent

concentration C1 in the supply water of the first reverse osmosis membrane device 12 was 3 mg/L, the amount of antimicrobial agent added X2 was 91.5 g/d, and the antimicrobial agent concentration C2 was 40.8 mg/L (> 3 mg/L). In comparison to Comparative Example 2-2, the amount of antimicrobial agent added in Comparative Example 2-1 was increased by 76.4 g/d. The result is shown in Table 2.

[0080]

[Table 2]

Table 2: Test for investigating amount of antimicrobial agent added

	Antimicrobial agent	Rejection rate of antimicrobial agent by RO membrane [%]	Amount of antimicrobial agent added X1 [g/d]	Antimicrobial agent concentration C1 [mg/L]	Amount of antimicrobial agent added X2 [g/d]	Antimicrobial agent concentration C2 [mg/L]	Total amount of antimicrobial agent added X1+X2 [g/d]	Reduction in amount of antimicrobial agent [g/d]
Example 1-1	Hypobromous acid stabilized composition	99.1	-	3.0	14.5	6.1	14.5	7.0
Comparative Example 1-1			14.4	3.0	7.1	3.0	21.5	
Example 1-2	Isothiazolone	81.8	-	3.0	16.1	7.3	16.1	4.2
Comparative Example 1-2			14.4	3.0	5.9	3.0	20.3	
Example 1-3	Hypochlorous acid	71.0	-	3.0	17.8	8.3	17.8	1.7
Comparative Example 1-3			14.4	3.0	5.1	3.0	19.5	
Example 1-4	Halocyanoacetamide compound	97.0	-	3.0	14.6	6.2	14.6	6.8
Comparative Example 1-4			14.4	3.0	7.0	3.0	21.4	
Comparative Example 2-1	Chloramine	10.2	-	3.0	91.5	40.8	91.5	-76.4
Comparative Example 2-2			14.4	3.0	0.7	3.0	15.1	

Amount of supply water Q = 200 L/h

First stage RO membrane recovery rate = 50%

Second stage RO membrane recovery rate = 90%

[0081]

<Example 2 and Comparative Example 3>

Testing was performed using chlorosulfamic acid (anionic) as the antimicrobial agent, using the water treatment system of FIG. 1 in Example 2, and using the conventional water treatment system of FIG. 3 in Comparative Example 3.

[0082]

[Example 2-1 and Comparative Example 3-1]

In Example 2-1 and Comparative Example 3-1, the reverse osmosis membrane “ES20”, which is an anionically-charged membrane manufactured by Nitto Denko Corporation, was used as the first stage and second stage reverse osmosis membranes. At this time, measurement of the rejection rate of chlorosulfamic acid by the reverse osmosis membrane revealed a value of 99.6%.

[0083]

In Comparative Example 3-1, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, the amount of antimicrobial agent added ($X1 + X2$) was 21.6 g/d. Next, in Example 2-1, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent concentration C1 in the supply water of the first reverse osmosis membrane device was 3 mg/L, the amount of antimicrobial agent added X2 was 14.4 g/d, and the antimicrobial agent concentration C2 was 6.0 mg/L (> 3 mg/L). In comparison to Comparative Example 3-1, the amount of antimicrobial agent added in Example 2-1 was reduced by 7.2 g/d. The result is shown in Table 3.

[0084]

[Example 2-2 and Comparative Example 3-2]

In Example 2-2 and Comparative Example 3-2, the reverse osmosis membrane “ES20”, which is an anionically-charged membrane manufactured by Nitto Denko

Corporation, was used as the first stage reverse osmosis membrane, and “LFC3”, which is a neutral membrane manufactured by Nitto Denko Corporation, was used as the second stage reverse osmosis membrane. At this time, measurement of the rejection rate of chlorosulfamic acid by the reverse osmosis membrane revealed a value of 97.9%.

5 [0085]

In Comparative Example 3-2, when the antimicrobial agent was added such that, in terms of the antimicrobial agent concentration C1 added from the injection point 1 and the antimicrobial agent concentration C2 added from the injection point 2, the antimicrobial agent concentrations C1 and C2 were both 3 mg/L, and the amount of antimicrobial agent added ($X1 + X2$) was 21.4 g/d. Next, in Example 2-2, when the antimicrobial agent was added from the injection point 2 such that the antimicrobial agent concentration C1 in the supply water of the first reverse osmosis membrane device 12 was 3 mg/L, the amount of antimicrobial agent added X2 was 14.5 g/d, and the antimicrobial agent concentration C2 was 6.1 mg/L (> 3 mg/L). In comparison to Comparative Example 3-2, the amount of antimicrobial agent added in Example 2-2 was reduced by 6.9 g/d, and the magnitude of the reduction was smaller than that between Comparative Example 3-1 and Example 2-1. The result is shown in Table 3.

[0086]

[Table 3]

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Table 3: Test for investigating RO membrane type

	RO membrane	Rejection rate of antimicrobial agent by RO membrane [%]	Amount of antimicrobial agent added X1 [g/d]	Antimicrobial agent concentration C1 [mg/L]	Amount of antimicrobial agent added X2 [g/d]	Antimicrobial agent concentration C2 [mg/L]	Total amount of antimicrobial agent added X1+X2 [g/d]	Reduction in amount of antimicrobial agent [g/d]
Example 2-1	Anionically-charged membrane	99.6	-	3.0	14.4	6.0	14.4	7.2
Comparative Example 3-1			14.4	3.0	7.2	3.0	21.6	
Example 2-2	Neutral membrane	97.9	-	3.0	14.5	6.1	14.5	6.9
Comparative Example 3-2			14.4	3.0	7.0	3.0	21.4	

Antimicrobial agent: chlorosulfamic acid

Amount of supply water Q = 200 L/h

First stage RO membrane recovery rate = 50%

Second stage RO membrane recovery rate = 90%

5

[0087]

From the testing above, the amount of reduction in the antimicrobial agent was greater for the examples than the comparative examples.

[0088]

5 In this manner, the amount of antimicrobial agent added in a water treatment using two or more stages of reverse osmosis membranes was able to be reduced by using the water treatment system and the water treatment method described in the examples.

10

REFERENCE SIGNS LIST

[0089]

1, 3, 5: Water treatment system

10: Raw water tank

12: First reverse osmosis membrane device

15 14: Second reverse osmosis membrane device

16, 18, 20, 22, 24: Line

26: Circulation line

28, 32: Antimicrobial agent addition line

30: Degassing membrane

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CLAIMS

1. A water treatment system using two or more stages of reverse osmosis membranes, the water treatment system comprising at least
 - a first stage reverse osmosis membrane device,
 - a second stage reverse osmosis membrane device for treating a permeate of the first stage reverse osmosis membrane device, and
 - a circulation mechanism for circulating a concentrate of the second stage reverse osmosis membrane device to a supply water of the first stage reverse osmosis membrane device,wherein an antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90% is added to a supply water of the second stage reverse osmosis membrane device;
 - wherein the antimicrobial agent is not added to the supply water of the first stage reverse osmosis membrane device other than the antimicrobial agent contained in the concentrate;
 - wherein the concentrate of the first stage reverse osmosis membrane device is discharged.
2. The water treatment system according to Claim 1, wherein
 - the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90% is at least one of a hypobromous acid stabilized composition, chlorosulfamic acid, and a halocynoacetamide compound.
3. The water treatment system according to Claim 1 or 2, wherein
 - a degassing membrane for degassing the supply water of the second stage reverse osmosis membrane is provided at a stage subsequent to addition of the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90%.

4. The water treatment system according to any one of Claims 1 to 3, wherein
the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90% is an anionic antimicrobial agent, and
the second stage reverse osmosis membrane device comprises an anionically-charged membrane.
5. The water treatment system according to Claim 4, wherein
the first stage reverse osmosis membrane device comprises a neutral membrane.
6. A water treatment method for performing two or more stages of reverse osmosis membrane treatment using at least a first stage reverse osmosis membrane, and a second stage reverse osmosis membrane for treating a permeate of the first stage reverse osmosis membrane, the method comprising
using a concentrate of the second stage reverse osmosis membrane by circulating the concentrate to a supply water of the first stage reverse osmosis membrane, and
adding an antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90% to a supply water of the second stage reverse osmosis membrane,
wherein the antimicrobial agent is not added to the supply water of the first stage reverse osmosis membrane other than the antimicrobial agent contained in the concentrate;
wherein the concentrate of the first stage reverse osmosis membrane is discharged.
7. The water treatment method according to Claim 6, wherein
the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90% is at least one of a hypobromous acid stabilized composition, chlorosulfamic acid, and a halocynoacetamide compound.
8. The water treatment method according to Claim 6 or 7, wherein

the supply water of the second stage reverse osmosis membrane is degassed using a degassing membrane at a stage subsequent to addition of the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90%.

9. The water treatment method according to any one of Claims 6 to 8, wherein
the antimicrobial agent having a rejection rate by a reverse osmosis membrane of at least 90% is an anionic antimicrobial agent, and
the second stage reverse osmosis membrane is an anionically-charged membrane.
10. The water treatment method according to Claim 9, wherein
the first stage reverse osmosis membrane is a neutral membrane.