

DESCRIPTION

TITLE

5 METHOD OF CLEANING SEPARATION MEMBRANE OR
CONCENTRATION MEMBRANE AND CLEANING DEVICE

TECHNICAL FIELD

[0001] The present disclosure relates to a method of cleaning a separation
membrane or a concentration membrane and a cleaning device.
10

BACKGROUND

[0002] When a membrane is used to perform separation or concentration,
adhered material contained in a liquid that is a subject of the separation or
concentration or adhered material produced through a reaction at a surface or
15 inner part of the membrane during the separation or concentration may be
deposited at the surface or inner part of the membrane, thereby reducing
permeability of the membrane. By cleaning the surface or inner part of the
membrane either periodically or when permeability decreases, it is possible to
maintain permeability while performing separation or concentration.

20 Cleaning is an operation of removing adhered material from a
membrane, and an essential condition thereof is that the cleaning does not
damage the membrane or other members.

Cleaning of a membrane may be categorized according to the size with
which adhered material is stripped from the membrane. That is to say, cleaning
25 may be categorized as methods in which foulants are separated as solid masses,
methods in which foulants are dissolved, and methods in which intense
cleaning is performed to cause decomposition of foulants from the molecular
structure thereof.

A method in which foulants are separated as solid masses takes a
30 surfactant as a mechanism and has comparatively mild conditions that are not
degrading with respect to the material of a membrane. A method in which
foulants are dissolved takes any of various acids, alkalis, oxidants, reductants,
EDTA, etc. as a mechanism and has a cleaning effect through increasing water
solubility. A method in which foulants are decomposed takes a strong alkali
35 such as caustic soda or an oxidant such as sodium hypochlorite as a mechanism
and has harsh conditions that cause deterioration of strength of the material of

a membrane.

Although adhered material on a membrane may be just a single substance, cases in which various types of substances are adhered are common. For example, a combination of cleaning by an acid and cleaning by an alkali
5 may be adopted in the case of adhesion of either of inorganic material or organic material.

[0003] As one example of chemical cleaning of a membrane, there is a known method of treating chemical cleaning waste liquid in which a first step is performed using a mixed solution of sodium hydroxide and sodium
10 hypochlorite as a cleaning chemical liquid and a second step is performed using a reductive acid solution such as sodium bisulfite solution, sodium hydrogen sulfite solution, sodium sulfite solution, or sodium thiosulfate solution as a cleaning chemical liquid (Patent Literature (PTL) 1).

[0004] In another known method, a filter is installed in a pipe when cleaning
15 of a membrane module is to be performed so as to prevent re-adhesion of contaminants that have been stripped from the membrane (PTL 2). No specific limitations are placed on chemical cleaning in this method, and it is disclosed that a combination of acid cleaning using an acid such as hydrochloric acid, sulfuric acid, nitric acid, citric acid, or oxalic acid and alkali cleaning using an
20 alkali such as caustic soda or sodium hypochlorite, hydrogen peroxide water, a surfactant, or the like may be used.

[0005] A chemical liquid cleaning method for a membrane module in which cleaning with purified water follows chemical cleaning has also been proposed, and in this method, purified water used in cleaning that has been discharged
25 from the membrane module is treated in a recovery membrane module and is then reused (PTL 3). This document does not place any specific limitations on the chemical liquid and discloses that an inorganic acid aqueous solution such as hydrochloric acid, nitric acid, sulfuric acid, or hydrofluoric acid, an organic acid aqueous solution such as citric acid or oxalic acid, an oxidant or reductant
30 such as a hypochlorite salt aqueous solution, hydrogen peroxide water, or a bisulfite salt, an aqueous solution of a detergent or a surfactant, or the like may be used.

Non-Patent Literature (NPL) 1 is a review paper that comprehensively describes various types of membranes and cleaning chemicals used for cleaning
35 these various types of membranes.

CITATION LIST

Patent Literature

[0006] PTL 1: JP 2005-193119 A

PTL 2: JP 2006-281022 A

5 PTL 3: JP 2005-246361 A

Non-Patent Literature

[0007] NPL 1: Ram Chandra Bogati, Membrane Fouling and Its Control in Drinking Water Membrane Filtration Process, 2014

10 SUMMARY

(Technical Problem)

[0008] In some instances, the methods described in PTL 1 to 3 have not enabled sufficient removal of deposits that are strongly adhered to a membrane surface and have not been able to restore membrane permeability. Moreover,
15 sodium hypochlorite that is described in the aforementioned patent literature is problematic in that it reduces the strength of constituent members of a membrane module and may lead to issues such as membrane rupture when a membrane module is used for a long time.

Furthermore, sodium hypochlorite that is described in PTL 1 to 3 and
20 NPL 1 is problematic in that it reduces the strength of constituent members of a membrane module and may lead to issues such as membrane rupture when a membrane module is used for a long time.

The inventor discovered that, as an effective means of removing adhered material from a membrane, setting a cleaning liquid to alkaline and
25 reducing conditions enables dissolution of adhered material, does not cause oxidation deterioration of a material used as a membrane material, and does not present any concerns of deterioration in long-term use, thus leading to the present disclosure.

[0009] An object of the present disclosure is to provide a method of cleaning
30 a membrane that can remove deposits adhering to a membrane surface, can restore permeability of the membrane, can maintain filtration and concentration performance of the membrane, and does not cause deterioration of strength of a member that is a constituent of a membrane module.

(Solution to Problem)

35 **[0010]** Specifically, the present disclosure is as set forth below.

[1]

A method of cleaning a separation membrane or a concentration membrane comprising a cleaning step of bringing a reduction cleaning liquid into contact with a separation membrane or a concentration membrane at a pH of 7.0 or higher.

5 [2]

The method of cleaning a separation membrane or a concentration membrane according to [1], wherein the reduction cleaning liquid has a redox potential of -300 mV or less.

[3]

10 The method of cleaning a separation membrane or a concentration membrane according to [1] or [2], wherein the reduction cleaning liquid has a pH of not lower than 7.0 and not higher than 14.0.

[4]

15 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [3], wherein the reduction cleaning liquid has a redox potential of not less than $-1,200$ mV and not more than -500 mV.

[5]

20 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [4], wherein

the reduction cleaning liquid contains a reductant and an alkali,

the reductant is one or more selected from the group consisting of sodium hydrosulfite, thiourea dioxide, borohydrides, and sodium formaldehyde sulfoxylate, and

25 the alkali is one or more selected from the group consisting of sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, and sodium bicarbonate.

[6]

30 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [5], wherein the cleaning step is performed at a temperature of 1°C to 100°C .

[7]

35 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [6], wherein the reduction cleaning liquid further contains a surfactant.

[8]

The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [7], wherein

the separation membrane or the concentration membrane is a hollow fiber membrane or a flat sheet membrane,

5 the separation membrane or the concentration membrane is housed inside of a case,

a module having the separation membrane or the concentration membrane housed inside of the case is a case-type module, and

10 the cleaning step is a step of filling the reduction cleaning liquid into the case and bringing the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

[9]

The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [8], wherein

15 the separation membrane or the concentration membrane is a hollow fiber membrane or a flat sheet membrane,

the separation membrane or the concentration membrane is housed inside of a case,

20 a module having the separation membrane or the concentration membrane housed inside of the case is a case-type module, and

the cleaning step is a step of causing the reduction cleaning liquid to pass through a surface and an inner part of the separation membrane or the concentration membrane and bringing the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

25 [10]

The method of cleaning a separation membrane or a concentration membrane according to [8], wherein the case-type module is an external pressure filtration type.

[11]

30 The method of cleaning a separation membrane or a concentration membrane according to [9], wherein the case-type module is an external pressure filtration type.

[12]

35 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [11], wherein the separation membrane or the concentration membrane is a membrane for separation or

concentration in a wastewater treatment process, a water purification process, or a seawater desalination process.

[13]

5 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [12], wherein the separation membrane or the concentration membrane is a UF membrane, an MF membrane, an RO membrane, an FO membrane, or an NF membrane.

[14]

10 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [13], wherein the separation membrane or the concentration membrane is a membrane that contains one or more resins selected from the group consisting of PVDF, PE, PSF, PAN, PP, PTFE, ETFE, PA, and PES as a constituent component.

[15]

15 The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [14], wherein the cleaning step is a step of bringing one or more selected from the group consisting of an internal surface, an external surface, and an inner part of the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

20 [16]

The method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [15], wherein the separation membrane or the concentration membrane is a membrane that has been used to separate or concentrate a solution after aerobic biological treatment.

25 [17]

A cleaning method comprising a step of bringing a reduction cleaning liquid into contact with a separation membrane or a concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when, in operation of a device including the separation membrane or the concentration membrane, there is satisfaction of any one of a situation in which a predefined operating pressure has been reached, a situation in which a predefined operating pressure rise has been reached, a situation in which a predefined operating time has been reached, a situation in which a change to a predefined separation or concentration subject state has occurred, and a
30 situation in which a decrease to a predefined separation or concentration
35 membrane permeability has occurred.

[18]

The cleaning method according to [17], comprising a step of bringing a reduction cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation
5 membrane or the concentration membrane when there is satisfaction of any one of a situation in which the predefined operating pressure has been reached, a situation in which the predefined operating pressure rise has been reached, a situation in which the predefined operating time has been reached, a situation in which a change to the predefined separation or concentration subject state
10 has occurred, and a situation in which a decrease to the predefined separation or concentration membrane permeability has occurred and there is also satisfaction of any one of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second
15 operating time has been reached, a situation in which a change to a predefined second separation or concentration subject state has occurred, and a situation in which a decrease to a predefined second separation or concentration membrane permeability has occurred.

[19]

20 A cleaning device used in the method of cleaning a separation membrane or a concentration membrane according to any one of [1] to [18], comprising a section where the separation membrane or the concentration membrane and the reduction cleaning liquid are brought into contact.

[20]

25 A device comprising a separation membrane or a concentration membrane, wherein the device brings a reduction cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when there is satisfaction of any one of a situation in which a predefined operating
30 pressure has been reached, a situation in which a predefined operating pressure rise has been reached, a situation in which a predefined operating time has been reached, a situation in which a change to a predefined separation or concentration subject state has occurred, and a situation in which a decrease to a predefined separation or concentration membrane permeability has occurred.

35 [21]

The device according to [20], wherein the device brings a reduction

cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when there is satisfaction of any one of a situation in which the predefined operating pressure has been reached, a situation in which
5 the predefined operating pressure rise has been reached, a situation in which the predefined operating time has been reached, a situation in which a change to the predefined separation or concentration subject state has occurred, and a situation in which a decrease to the predefined separation or concentration membrane permeability has occurred and there is also satisfaction of any one
10 of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second operating time has been reached, a situation in which a change to a predefined second separation or concentration subject state has occurred, and a situation in which a decrease to
15 a predefined second separation or concentration membrane permeability has occurred.

(Advantageous Effect)

[0011] As a result of having the configuration set forth above, the method of cleaning a membrane according to the present disclosure can remove deposits
20 adhered to a membrane surface and restore permeability of the membrane, can maintain filtration and concentration performance of the membrane, and can clean the membrane without causing deterioration of strength of a member that is a constituent of a membrane module.

25 BRIEF DESCRIPTION OF THE DRAWINGS

[0012] In the accompanying drawings:

FIG. 1 is a conceptual diagram of maintenance cleaning and recovery cleaning;

FIG. 2 is a diagram of EDX analysis results of a membrane used in
30 Examples 1 to 3 and Comparative Examples 1 to 5;

FIG. 3 is a diagram of EDX analysis results of Comparative Example 2;

FIG. 4 is a diagram of EDX analysis results of Comparative Example 3;

35 FIG. 5 is a diagram of EDX analysis results of Example 2;

FIG. 6 is a diagram of EDX analysis results of Example 3;

FIG. 7 is a diagram for describing a wastewater treatment process in Examples 10 and 11 and Comparative Examples 9 and 10;

FIG. 8 is a diagram for describing warm water bathing in Example 10, etc.; and

5 FIG. 9 is a diagram for describing cleaning liquid circulation in Example 11, etc.

DETAILED DESCRIPTION

10 **[0013]** The following provides a detailed description of an embodiment of the present disclosure (hereinafter, referred to as the “present embodiment”). Note that the present embodiment is an example for describing the present disclosure and that the present disclosure is not limited to just this embodiment. In other words, various modifications can be made to the present disclosure that do not deviate from the essence thereof.

15 **[0014]** {Method of cleaning separation membrane or concentration membrane}

A method of cleaning a membrane of the present embodiment includes a cleaning step of bringing a reduction cleaning liquid into contact with a separation membrane or a concentration membrane at a pH of 7.0 or higher.

20 **[0015]** [Separation membrane and concentration membrane]

Although no specific limitations are placed on the separation membrane and the concentration membrane so long as they are membranes that are used in separation or concentration, separation membranes that perform separation or concentration through pressure require more effective cleaning because adhered material is readily deposited at a surface of the membrane and because such separation membranes are required to operate continuously while filtration and cleaning are repeated. The separation membrane or the concentration membrane may be an ultrafiltration membrane (UF membrane), a microfiltration membrane (MF membrane), a nanofiltration membrane (NF
25 membrane), or a reverse osmosis membrane (RO membrane), and these membranes can be effectively used in the cleaning method of the present embodiment.

An OARO membrane (osmosis-assisted reverse osmosis membrane) is a concentration system that utilizes osmotic pressure difference in addition to
35 filtration pressure by causing at least some of a liquid that has been concentrated to flow at a secondary side. An OARO membrane is also

susceptible to deposition of adhered material and requires cleaning in the same manner as a filtration membrane since it is the same in terms that pressure is applied to the membrane surface, and hence an OARO membrane can be effectively used in the cleaning method of the present embodiment.

5 A forward osmosis membrane (FO membrane) is a membrane that is used in separation/concentration where only a solvent such as water migrates as a result of a draw solution having high osmotic pressure flowing at a secondary side of the membrane. Although such a membrane does not experience deposition due to pressure since pressure does not act on the
10 membrane, an FO membrane can still be effectively used in the cleaning method of the present embodiment since precipitation may occur at the membrane surface due to concentration polarization.

 A membrane distillation membrane (MD membrane) is a membrane with which only vapor having high saturated vapor pressure from a liquid
15 flowing at the primary side of the membrane migrates to the secondary side and that does not require pressure. Although this means that there is a low tendency for deposition of adhered material on the surface at the primary side of the membrane, cleaning is still necessary because precipitation of scale or the like can occur during long-term use, and hence an MD membrane can be
20 effectively used in the cleaning method of the present embodiment.

 An RO membrane, NF membrane, OARO membrane, or FO membrane may typically be what is referred to as a composite semipermeable membrane where a thin membrane of an aromatic polyamide is formed on a substrate membrane surface layer such as a UF membrane and where this membrane acts
25 as the separation mechanism. Aromatic polyamides are susceptible to deterioration by oxidation, precluding the use of sodium hypochlorite, which is a representative example used to perform cleaning by oxidation. In this regard, the reduction cleaning liquid that is used in the cleaning method of the present embodiment does not cause deterioration of aromatic polyamides and
30 thus can serve as an effect cleaning method.

 Such composite semipermeable membranes are used in wastewater treatment and seawater desalination for obtaining high-purity water because they enable separation or concentration at the molecular level. In pre-treatment of a composite semipermeable membrane, a process in which a membrane
35 having a larger pore size is provided so as to reduce fouling of the composite semipermeable membrane is typically adopted. Since a trace amount of a

component of a cleaning liquid may remain in a pre-treatment membrane after cleaning of the pre-treatment membrane, trouble can arise when operation restarts because a trace amount of the cleaning liquid may reach the composite semipermeable membrane and cause oxidation deterioration. However, the
5 reduction cleaning liquid described above does not have a concern of indirectly damaging a composite semipermeable membrane when it is used in cleaning of a pre-treatment membrane for the composite semipermeable membrane. Accordingly, a pre-treatment membrane for a composite semipermeable membrane is a suitable membrane for the present cleaning liquid.

10 The separation membrane or the concentration membrane is preferably a UF membrane, an MF membrane, an RO membrane, an FO membrane, or an NF membrane.

Note that the ultrafiltration membrane may be a membrane having a pore diameter of 0.001 μm to 0.01 μm (for example, a membrane that can block
15 particles of 2 nm to 0.1 μm). The ultrafiltration membrane may have a molecular weight cut off of 1,000 to 150,000.

Moreover, the microfiltration membrane is a membrane that has a pore diameter of tens of nanometers to approximately 10 μm and that can block particles that are larger than 0.1 μm .

20 Furthermore, the nanofiltration membrane may be a membrane that has a pore diameter of 0.0005 μm or less and refers to a membrane that can block particles of 1 nm or less.

Note that the molecular weight cut off refers to a value that is measured by a method of determining a removal ratio when a solution containing a
25 standard substance (dextran, insulin, etc.) of known molecular weight is separated by the membrane.

The RO membrane, NF membrane, and FO membrane each have a nano-level separation size. In contrast to the RO membrane, which has the ability to block all electrolyte ions, the NF membrane is a membrane that can only block
30 divalent inorganic ions. Moreover, in contrast to the RO membrane and NF membrane, which have a membrane structure where permeated water is obtained with pressure as a driving force, the FO membrane is a membrane having permeation of water due to osmotic pressure difference of two liquids via an aromatic polyamide layer as a principle and has a membrane structure
35 that does not require pressure resistance.

[0016] The separation membrane or the concentration membrane may be an

organic membrane or may be an inorganic membrane.

The organic membrane may be a membrane in which a resin is used (for example, a membrane in which the mass proportion of the resin relative to 100 mass% of the membrane is 90 mass% or more (preferably 95 mass% or more)). The resin may be a fluoro-resin including one or more selected from the group consisting of a vinylidene fluoride resin (PVDF), a chlorotrifluoroethylene resin (PCTFE), a tetrafluoroethylene resin (PTFE), an ethylene-tetrafluoroethylene copolymer (ETFE), an ethylene-monochlorotrifluoroethylene copolymer (ECTFE), a hexafluoropropylene resin (HFP), and mixtures of these resins; a polysulfone-based resin including one or more selected from the group consisting of polysulfone (PSF), polyethersulfone (PES), sulfonated polyethersulfone (S-PES), sulfonated polysulfone (S-PSF), and mixtures of these resins; a polyolefinic resin including one or more selected from the group consisting of polyethylene (PE), polypropylene (PP), polybutene (PB), a polymethylpentene resin (PMP), a cycloolefin resin (COP), and mixtures of these resins; a polyacrylonitrile-based resin including one or more selected from the group consisting of an acrylonitrile resin such as polyacrylonitrile (PAN), an acrylonitrile-based copolymer resin, and mixtures of these resins; a polyamide resin (PA); cellulose; cellulose triacetate; or the like. The resin may be one type of resin or a combination of a plurality of types of resins. The resin preferably includes one or more selected from the group consisting of PVDF, PE, PSF, PAN, PP, PTFE, ETFE, PA, and PES, and is more preferably just one selected from the group consisting of PVDF, PE, PSF, PAN, PP, PTFE, ETFE, PA, and PES. The organic membrane may be a composite membrane structure having a membrane layer formed on a reinforcing material such as non-woven fabric or braided cord.

The inorganic membrane may be a ceramic membrane having a metal oxide such as alumina, mullite, titania, or zirconia as a raw material.

[0017] The separation membrane or the concentration membrane is preferably an organic membrane containing one or more resins selected from the group consisting of PVDF, PE, PSF, PAN, PP, PTFE, ETFE, PA, and PES from viewpoints of membrane strength, uniformity of pore diameter, and ease of handling.

[0018] In terms of form, the separation membrane or the concentration membrane may be a hollow fiber membrane, a tubular membrane, a flat sheet

membrane, or the like, and is preferably a hollow fiber membrane or a flat sheet membrane. The hollow fiber membrane may be a membrane having an external diameter of not less than 0.5 mm and not more than 5 mm, with an external diameter of not less than 0.7 mm and not more than 3 mm being more preferable, and an external diameter of not less than 1.0 mm and not more than 2.0 mm even more preferable. A hollow fiber membrane is a form having many merits from perspectives such as ease of use and reduction of device cost since it can provide the highest membrane area per installation area and thereby enables a more compact filtration system or concentration system. In the case of an inorganic membrane, a tubular, monolithic, or plate-type form may be adopted, for example.

[0019] The separation membrane or the concentration membrane may be of an immersion type that is used in an immersed state without housing in a case or may be housed inside of a case.

In a situation in which the separation membrane or the concentration membrane is housed inside of a case, a module having the separation membrane or the concentration membrane housed inside of the case may be a case-type module. In particular, a case-type module that enables increased flux through operation under high pressure is preferable. The case-type module is preferably a case-type module having a hollow fiber membrane or a flat sheet membrane housed inside of a case. For example, the case-type module may be a module that includes a hollow fiber membrane bundle in which a plurality of hollow fiber membranes are bundled together and a tube-shaped housing accommodating the hollow fiber membrane bundle.

The case-type module may be a hollow fiber membrane type, a type in which tubular membranes of larger diameter than hollow fiber membranes are packed, a spiral type in which a flat sheet membrane is wound up, a pleated type in which a flat sheet membrane is folded up, a disk type in which a plurality of flat sheet membranes are stacked, or the like.

Filtration by a case-type module in which the above-described hollow fiber membrane is used may be a dead-end filtration or external pressure process. From a viewpoint of membrane area where filtration is performed, an external pressure-type module that performs filtration at an external surface of a membrane is preferable.

[0020] Examples of membrane cleaning include maintenance cleaning and recovery cleaning illustrated in FIG. 1. Maintenance cleaning is normally

cleaning in which a cleaning liquid of weak concentration is brought into contact with a membrane for a short time each time a fixed period passes, for example, in order to delay a rise of operating pressure. By increasing the number of times that cleaning is performed using a low-concentration cleaning liquid at a point at which there is light membrane fouling, it is possible to inhibit membrane fouling even though the amount of cleaning recovery per one clean is small.

Recovery cleaning is cleaning that is performed once permeability has decreased, such as when the operating pressure has reached an implementation pressure. Recovery cleaning requires a high cleaning liquid concentration since the degree of fouling is high, and cleaning with a higher pH and a lower redox potential facilitates recovery.

The maintenance cleaning and recovery cleaning described above can be performed manually or automatically, and the aforementioned reduction cleaning liquid can be used in both maintenance cleaning and recovery cleaning.

Particularly in a case in which maintenance cleaning or recovery cleaning is performed automatically, cleaning with the reduction cleaning liquid is implemented automatically upon satisfaction of any one of conditions of a predefined operating pressure, a predefined operating pressure rise, a predefined operating time, a predefined feed water state change, a change to a predefined separation or concentration subject state, and a decrease to a predefined separation membrane or concentration membrane permeability. The recovery cleaning is cleaning that is performed automatically in any one of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second operating time has been reached, a situation in which a change to a predefined second separation or concentration subject state has occurred, and a situation in which a decrease to a predefined second separation or concentration membrane permeability has occurred, where these situations differ from the conditions described above.

[0021] The separation membrane or the concentration membrane is not specifically limited so long as it is a membrane that has been used in separation or concentration, but is preferably a membrane having contaminants adhered to a membrane surface. The separation membrane or the concentration membrane is preferably a membrane having waste liquid adhered to a membrane surface that has been used for separation or concentration in a

wastewater treatment process, a water purification process, or a seawater desalination process. In particular, a membrane that has been used for separation or concentration of a solution after a process of performing biological treatment (preferably aerobic biological treatment or aerobic
5 biological treatment using activated sludge) in a wastewater treatment process is more preferable as a cleaning subject membrane since adhered material at the membrane surface is often oxidized and the cleaning effect of the aforementioned reduction cleaning liquid readily acts thereon. The separation membrane or the concentration membrane is preferably a membrane that has
10 been used in separation or concentration of a solution after aerobic biological treatment. The membrane that has been used in separation or concentration of a solution after aerobic biological treatment may be a membrane having a biopolymer produced through biological treatment such as aerobic biological treatment adhered thereto, for example. The inventor and others discovered
15 that biopolymers produced through biological treatment are particularly easy to clean using the aforementioned reduction cleaning liquid, presumably since such biopolymers are typically adhered through physical pressing against a membrane rather than through chemical bonding with the membrane.

[0022] The contaminants that are adhered to the membrane surface (for
20 example, contaminants that adhere to the membrane surface during the aforementioned wastewater treatment process, water purification process, or seawater desalination process) may be suspended matter of organic material or inorganic material or dissolved organic polymers that are contained in river water, lake water, subterranean water, feed water for industry, sewage, sewage
25 secondary treatment water, industrial wastewater, domestic wastewater, seawater, dyeing wastewater, etc., precipitated material resulting from precipitation of components that have dissolved at the membrane surface, or the like. Other examples include precipitated material contained in wastewater treatment in industrial fields such as valuable resource concentration of foods,
30 drinks, etc., the chemical industry, and petroleum refining.

Examples of membrane contaminants (foulants) also include suspended fine particles that are contained in wastewater, polymerized organic material and oils, inorganic material that has precipitated at the membrane surface, and composites of any thereof. Depending on the contaminant, there are cases in
35 which sufficient recovery is not achieved with representative cleaning agents such as a mixture of sodium hypochlorite and sodium hydroxide and inorganic

and organic acids such as hydrochloric acid and citric acid that are conventionally used for a membrane having polymerized organic material adhered to the membrane surface.

Studies conducted by the inventor revealed that a high cleaning effect is achieved and the original permeability of a membrane is restored by using a reduction cleaning liquid that displays reducing ability under alkaline conditions. In addition to the effect of dissolution of adhered organic material fouling that is originally achieved under alkaline conditions, the effect of dissolution is thought to be further enhanced through reducing action of a reductant changing the molecular structure of the adhered material.

The cleaning action of the reduction cleaning liquid restores permeability of the membrane between before and after cleaning through cleaning and yields an effect that oxygen atoms observed through elemental analysis of the membrane surface prior to cleaning are no longer observed after cleaning.

Particularly in the case of a wastewater treatment process, aerobic biological treatment is often performed (for example, aerobic treatment using activated sludge), and there may be exposure to a state in which the redox potential is from +50 mV to +150 mV for several hours during this aerobic biological treatment. Consequently, contaminants such as organic material and suspended particles in the wastewater are oxidized and are thought to be in a state that readily undergoes decomposition through reducing action by the reduction cleaning liquid, thus resulting in a large cleaning effect through the reduction cleaning liquid.

[0023] [Reduction cleaning liquid]

The reduction cleaning liquid is a cleaning liquid that provides electrons to contaminants adhered to the separation membrane or the concentration membrane and takes oxygen from the contaminants.

The reduction cleaning liquid preferably contains a reductant and an alkali, and more preferably further contains a surfactant. Moreover, the reduction cleaning liquid may contain a solvent, an additive, an enzyme, or the like in addition to the above-described components.

The reduction cleaning liquid may be a liquid composition that is composed of only a reductant and an alkali, may be a liquid composition that is composed of only a reductant, an alkali, and a solvent, or may be a liquid composition that is composed of only a reductant, an alkali, a surfactant, and

a solvent.

The reduction cleaning liquid of the present embodiment is preferably a cleaning liquid for a separation membrane or a concentration membrane that has a pH of 7.0 or higher and that contains at least one or more reductants
5 selected from the group consisting of sodium hydrosulfite, thiourea dioxide, borohydrides, and sodium formaldehyde sulfoxylate and one or more alkalis selected from the group consisting of sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, and sodium bicarbonate.

[0024] (Reductant)

10 The reductant may be a hydrosulfite, thiourea dioxide, sodium borohydride, sodium formaldehyde sulfoxylate, or the like. In particular, one or more selected from the group consisting of sodium hydrosulfite, thiourea dioxide, borohydrides, and sodium formaldehyde sulfoxylate are preferable, and hydrosulfites and thiourea dioxide are more preferable in terms of cleaning
15 effect and time required for cleaning.

[0025] The mass proportion of the reductant relative to 100 mass% of the reduction cleaning liquid is preferably 0.02 mass% or more, more preferably 0.05 mass% to 10 mass%, and even more preferably 0.1 mass% to 5 mass% from a viewpoint that deterioration of strength of a membrane or module is
20 unlikely to arise.

[0026] (Alkali)

The alkali is preferably an alkali that can maintain the pH during the cleaning step at 7.0 or higher, and is more preferably an alkali that can maintain the pH of the reduction cleaning liquid at 7.0 or higher. The alkali may be a
25 mixture or may be a single compound, and examples thereof include sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, sodium bicarbonate, and lithium hydroxide. In particular, one or more selected from the group consisting of sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, and sodium bicarbonate are preferable, and
30 sodium hydroxide, sodium carbonate, potassium hydroxide, and mixtures thereof are more preferable from a viewpoint that contaminants adhered to a membrane surface are even more easily removed and even better recovery of water permeability after cleaning is achieved.

[0027] The mass proportion of the alkali relative to 100 mass% of the reduction cleaning liquid is preferably 0.02 mass% or more, more preferably
35 0.05 mass% to 10 mass%, and even more preferably 0.1 mass% to 5 mass%

from a viewpoint that deterioration of strength of a membrane or module is unlikely to arise.

[0028] (Surfactant)

The surfactant may be a non-ionic surfactant, an anionic surfactant, a cationic surfactant, or an amphoteric surfactant. In particular, a non-ionic surfactant or an anionic surfactant is preferable from a viewpoint that when such a surfactant is used in combination with the reductant and the alkali described above, contaminants are even more easily removed from a membrane surface and even greater recovery of water permeability after cleaning is achieved. In addition to cleaning effect, lack of foaming and ease of rinsing enabling washing out with only a small amount of cleaning are also important in selection of the surfactant.

[0029] The mass proportion of the surfactant relative to 100 mass% of the reduction cleaning liquid is preferably 0.01 mass% to 5.0 mass%, more preferably 0.02 mass% to 4.0 mass%, and even more preferably 0.05 mass% to 3.0 mass% in terms of cleaning effect and ease of foaming of the reduction cleaning liquid due to the surfactant.

[0030] (Solvent)

Water is preferable as the solvent from viewpoints such as solubility of the reductant and the alkali, permeability into a membrane as the reduction cleaning liquid, and solubility of adhered material that has been removed.

[0031] (Additives)

The reduction cleaning liquid may contain various additives that are commonly known. Examples of additives that can be used include emulsifiers, dispersants, chelating agents, and stabilizers.

[0032] (pH)

The pH when the reduction cleaning liquid is brought into contact with the separation membrane or the concentration membrane in the cleaning step is 7.0 or higher, and is preferably 7.0 to 14.0, more preferably 9.0 to 14.0, and even more preferably 10.0 to 14.0 in terms of even more easily removing contaminants adhered to a membrane surface to achieve even better recovery of water permeability after cleaning and in terms of further strengthening reducing power of the reductant.

The pH of the reduction cleaning liquid is preferably 7.0 or higher, more preferably 7.0 to 14.0, even more preferably 9.0 to 14.0, and particularly preferably 10.0 to 14.0 in terms of even more easily removing contaminants

adhered to a membrane surface to achieve even better recovery of water permeability after cleaning and in terms of further strengthening reducing power of the reductant.

Measurement of the pH can be performed using various types of pH
5 meters that are generally commercially available.

[0033] (Redox potential)

Redox potential is an indicator of reducing power of the reduction
cleaning liquid and can be measured by various measurement methods, such as
using an ORP meter. The redox potential of the reduction cleaning liquid is
10 preferably -300 mV or less, more preferably less than -300 mV, and even more
preferably less than -500 mV in terms of cleaning effect. Moreover, the redox
potential may be $-1,200$ mV or more.

In particular, it is preferable that the pH when the reduction cleaning
liquid is brought into contact with the separation membrane or the
15 concentration membrane in the cleaning step is 7.0 or higher (more preferably
7.0 to 14.0, and even more preferably 10.0 to 14.0) and that the redox potential
of the reduction cleaning liquid is -300 mV or less (more preferably not less
than $-1,200$ mV and less than -300 mV, and even more preferably not less than
 $-1,200$ mV and not more than -500 mV).

20 **[0034]** (Temperature)

The cleaning step is preferably performed at a temperature of 1°C to
 100°C , more preferably 5°C or higher, and even more preferably 10°C or higher
from a viewpoint that contaminants adhered to a membrane surface can be even
more easily removed and even better recovery of water permeability after
25 cleaning can be achieved. Moreover, in order to prevent damage caused by
thermal expansion or deformation of a member that is a constituent of a
membrane module, a temperature of 80°C or lower is more preferable, a
temperature of 60°C or lower is even more preferable, and a temperature of
 40°C or lower is particularly preferable.

30 **[0035]** (Time)

The time for which the separation membrane or the concentration
membrane is brought into contact with the reduction cleaning liquid in the
cleaning step may be 1 minute to 7 days, and is preferably 10 minutes to 3 days,
and more preferably 20 minutes to 1 day.

35 It is preferable that the separation membrane or the concentration
membrane is continuously brought into contact with the reduction cleaning

liquid in the cleaning step. A longer contact time means that a cleaning effect is achieved even with a weak reduction cleaning liquid concentration. In general, the cleaning effect can be interpreted to be: cleaning liquid concentration $\times$ cleaning time. For example, the same level of cleaning effect
5 may be considered to be obtained at a cleaning liquid concentration of $1/10^{\text{th}}$ through an immersion time that is 10 times as long. The time range should be from 1 to 100 times, with a more reliable range being from 1 to 50 times in length. The concentration should be from 1 to $1/100$, with a more reliable range being from 1 to $1/50$. However, a long cleaning time reduces time for separation
10 or concentration, and it is necessary to perform cleaning that also takes operation efficiency into consideration. The “concentration” refers mainly to concentrations of the reductant and the alkali.

[0036] A ratio of the internal/external area of the separation membrane or the concentration membrane relative to the mass of the reduction cleaning liquid
15 in the cleaning step is preferably $50 \text{ cm}^2/\text{g}$ or less, more preferably $30 \text{ cm}^2/\text{g}$ or less, and even more preferably $20 \text{ cm}^2/\text{g}$ or less from a viewpoint of cleaning efficiency.

Cleaning may also be implemented using another cleaning liquid after cleaning using the reduction cleaning liquid described above. Particularly
20 when adhered material that is adhered to a membrane surface contains a lot of inorganic components, cleaning using the reduction cleaning liquid may be followed by cleaning using an acid to enable further recovery of permeability of the membrane. Examples of acids that can be used include inorganic acids such as hydrochloric acid, nitric acid, and sulfuric acid and organic acids such
25 as citric acid, oxalic acid, and acetic acid.

[0037] The cleaning step is preferably a step of bringing one or more selected from the group consisting of one surface of the membrane (for example, an internal surface or an external surface of the membrane) and an inner part of the membrane into contact with the reduction cleaning liquid, and is more
30 preferably a step of bringing one surface of the membrane, both surfaces of the membrane, or both surfaces of the membrane and the inner part of the membrane into contact with the reduction cleaning liquid.

[0038] In the cleaning step, the membrane may be immersed in the reduction cleaning liquid, the membrane may be impregnated with the reduction cleaning
35 liquid, the reduction cleaning liquid may be circulated such that it flows at a surface and inner part of the membrane, or a combination thereof may be

adopted.

[0039] In a situation in which the membrane that has been used in separation or concentration and that is a subject of cleaning is a cartridge-type module, the membrane may be removed from a case and just that membrane may be cleaned or the membrane may be removed from a case, may be loaded into another case, and may then be cleaned in the cleaning step. Moreover, in a situation in which the membrane that has been used in separation or concentration and that is a subject of cleaning is not housed in a case, the membrane may be loaded into a case and may then be cleaned.

[0040] In a situation in which the membrane is a case-type module, it is preferable from a viewpoint of cleaning efficiency that the reduction cleaning liquid is filled into the case so as to bring the separation membrane or the concentration membrane into contact with the reduction cleaning liquid or that the reduction cleaning liquid is caused to pass through a surface and inner part of the separation membrane or the concentration membrane so as to bring the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

The method by which the reduction cleaning liquid is filled into the case may, for example, be a method in which the reduction cleaning liquid is loaded into the case and is then left at rest or is stirred by air bubbles through feeding of air into the case. During the above, it is preferable to control the temperature, pH, and redox potential to within the previously described preferable ranges.

The method by which the reduction cleaning liquid is caused to pass through a surface and inner part of the separation membrane or the concentration membrane may, for example, be a method in which the reduction cleaning liquid is caused to pass through an outer part or an inner part of a hollow fiber membrane in a case-type module. For example, since the reduction cleaning liquid flows along a membrane surface when pressure is not applied, it is possible to clean just the membrane surface without cleaning an inner part of the membrane, whereas application of pressure makes it possible to cause the reduction cleaning liquid to pass through the inner part of the membrane (i.e., to flow in the inner part of the membrane) and thereby also clean the inner part of the membrane.

[0041] In a situation in which the case-type module is an internal pressure filtration-type module, the reduction cleaning liquid may be caused to pass

from an inner part to an outer part of a hollow fiber membrane or may be caused to pass from an outer part to an inner part of a hollow fiber membrane, but it is preferable to cause the reduction cleaning liquid to pass from an outer part to an inner part of a hollow fiber membrane from a viewpoint of cleaning efficiency.

Moreover, with an external pressure filtration-type module, the reduction cleaning liquid may be caused to pass from an inner part to an outer part of a hollow fiber membrane or may be caused to pass from an outer part to an inner part of a hollow fiber membrane, but it is preferable to cause the reduction cleaning liquid to pass from an inner part to an outer part of a hollow fiber membrane from a viewpoint of cleaning efficiency.

When a chemical liquid is caused to flow at a surface and inner part of the membrane, it is possible to increase the flow rate up to the same maximum pressure as during normal filtration or concentration operation.

[0042] The cleaning step can be ended by stopping contact between the separation membrane or the concentration membrane and the reduction cleaning liquid.

[0043] Through the cleaning method of the present embodiment, it is possible to wash off contaminants that are adhered to a surface or inner part of the membrane and maintain permeability of the membrane. Since organic material or inorganic material contained in a concentration subject in concentration of a valuable resource may cause fouling of a membrane, reduce permeability of the membrane, and lower separation/concentration functionality, cleaning can be performed to cause recovery.

The cleaning method of the present embodiment differs from cleaning of fibers or pulp, for example, in terms that it can dislodge contaminants adhered to the membrane even without exposure to high temperature. Although the details are not clear, contaminants adhered to the membrane are also thought to readily decompose through the reductant. Moreover, use in combination with a surfactant enables extremely efficient washing off of contaminants adhered to the membrane. The cleaning effect with respect to contaminants containing oxygen atoms, in particular, is excellent.

[0044] The cleaning method of the present embodiment may, for example, be implemented by bringing the reduction cleaning liquid into contact with a provided membrane having contaminants adhered thereto so as to clean the membrane. Specifically, an appropriate amount (for example, the

aforementioned ratio of internal/external area of the separation membrane or concentration membrane relative to mass of the reduction cleaning liquid) of the reduction cleaning liquid may be brought into contact with a provided membrane having contaminants adhered thereto, circulation cleaning may be performed at the previously described temperature for the previously described time, and then a comparison of water permeability before and after cleaning (for example, a water permeability retention ratio subsequently described in the EXAMPLES section) may be made and presented to the provider of the membrane.

Note that waste liquid from cleaning may be treated as industrial waste liquid or may be neutralized with hydrochloric acid or the like and then be returned and gradually released upstream of wastewater treatment equipment.

[0045] The cleaning method of the present embodiment preferably includes a step of bringing a reduction cleaning liquid into contact with a separation membrane or a concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when, in operation of a device including the separation membrane or the concentration membrane, there is satisfaction of any one of a situation in which a predefined operating pressure has been reached, a situation in which a predefined operating pressure rise has been reached, a situation in which a predefined operating time has been reached, a situation in which a change to a predefined separation or concentration subject state has occurred, and a situation in which a decrease to a predefined separation or concentration membrane permeability has occurred.

The step of bringing a reduction cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane may be the step that was described above.

In the present specification, any one of a situation in which a predefined operating pressure has been reached, a situation in which a predefined operating pressure rise has been reached, a situation in which a predefined operating time has been reached, a situation in which a change to a predefined separation or concentration subject state has occurred, and a situation in which a decrease to a predefined separation or concentration membrane permeability has occurred may also be referred to as a “first condition”.

It may be the case that a plurality of conditions are set as the first

condition and that cleaning is performed once one condition among the plurality of conditions has been satisfied. The first condition may be a condition for performing the previously described maintenance cleaning, for example.

5 **[0046]** The predefined operating pressure can be determined as appropriate depending on the used device and the used concentration membrane or separation membrane and may, for example, be set as 100 kPa. The predefined operating pressure may be set as a pressure that is 1.5 times the operating pressure when an unused separation membrane or concentration membrane is
10 installed and cleaning begins, or may be set as a pressure that is 2.0 times that operating pressure.

[0047] The predefined operating pressure rise can be determined as appropriate depending on the used device and the used concentration membrane or separation membrane and may, for example, be set as 100 kPa. The pressure
15 rise may be set as the difference between the operating pressure when an unused separation membrane or concentration membrane is installed and cleaning begins and a pressure value that is 1.5 times that operating pressure, or may be set as the difference between that operating pressure and a pressure value that is 2.0 times that operating pressure.

20 **[0048]** The predefined operating time can be determined as appropriate depending on the used device and the used concentration membrane or separation membrane and may, for example, be set as 48 hours from the start of use or from a previous clean.

[0049] The predefined separation or concentration subject state can be
25 determined as appropriate depending on the used device and the used concentration membrane or separation membrane. For example, the turbidity of the subject may be taken periodically or continuously, and cleaning may be performed upon reaching a certain turbidity or higher so as to prevent blocking of the membrane by suspended matter.

30 The certain turbidity or higher may, for example, be set as 100 NTU or more.

 The turbidity can be measured by a method of causing the subject to flow through a turbidity meter.

 Note that contaminants may be substances that adhere to the separation
35 membrane or the concentration membrane in the cleaning method of the present embodiment.

[0050] The predefined separation membrane or concentration membrane permeability can be calculated by the following formula (1) from a relationship between pressure applied across the membrane and the amount of permeated water.

5 Permeation performance (LMH/100 kPa) = {Total amount of water permeating in module (L/min) × 60 (min) × Temperature correction to volume at permeated water temperature of 25°C}/Membrane area of module (m²)/Filtration pressure (kPa) × 100 ... Formula (1)

10 The state may be set as a state in which the value of this permeation performance is 50 LMH/100 kPa or a state in which the permeation performance is 1/4 of its initial value, for example.

15 The total amount of water permeating in the module is the total amount of water permeating through all hollow fiber membranes that are included in the module. In a case in which a module is not used, for example, the total amount of water permeating the separation membrane or the concentration membrane may be adopted.

20 Moreover, the membrane area of the module refers to the total surface area of all hollow fiber membranes included in the module, and in the case of an external pressure-type module, for example, may be the total external surface area of all hollow fiber membranes. In a case in which a module is not used, the total surface area of the separation membrane or the concentration membrane may be adopted.

25 **[0051]** The cleaning method of the present embodiment preferably includes a step of bringing a reduction cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when there is satisfaction of any one of a situation in which the predefined operating pressure has been reached, a situation in which the predefined operating pressure rise has been reached, a situation in which the predefined operating time has been reached, a situation in which a change to the predefined separation or concentration subject state has occurred, and a situation in which a decrease to the predefined separation or concentration membrane permeability has occurred and there is also satisfaction of any one of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second operating time has been reached, a situation in which a change to a

30

35

predefined second separation or concentration subject state has occurred, and a situation in which a decrease to a predefined second separation or concentration membrane permeability has occurred.

In the present specification, any one of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second operating time has been reached, a situation in which a change to a predefined second separation or concentration subject state has occurred, and a situation in which a decrease to a predefined second separation or concentration membrane permeability has occurred may also be referred to as a “second condition”.

It may be the case that a plurality of conditions are set as the second condition and that cleaning is performed once one condition among the plurality of conditions has been satisfied.

The first condition and the second condition are preferably the same parameter. For example, it is preferable for the first condition to be an operating pressure and the second condition to also be an operating pressure.

The second condition may be a condition for performing the previously described recovery cleaning, for example.

[0052] The second operating pressure may be the same as the predefined operating pressure described above or may be higher than that pressure.

The second operating pressure can be determined as appropriate depending on the used device and the used concentration membrane or separation membrane and may, for example, be set as 150 kPa. The second operating pressure may be set as a pressure that is 1.6 times the operating pressure when an unused separation membrane or concentration membrane is installed and cleaning begins, or may be set as a pressure that is 2.1 times that operating pressure.

In a case in which the first condition and the second condition are both operating pressures, the second operating pressure is preferably higher than the first operating pressure, more preferably at least 20 kPa higher than the first operating pressure, and even more preferably at least 50 kPa higher than the first operating pressure.

[0053] The second operating pressure rise may be the same as the predefined operating pressure rise described above or may be higher than that pressure rise.

The second operating pressure rise can be determined as appropriate depending on the used device and the used concentration membrane or separation membrane and may, for example, be set as 150 kPa. This pressure rise may be set as the difference between the operating pressure when an
5 unused separation membrane or concentration membrane is installed and cleaning begins and a pressure value that is 1.6 times that operating pressure, or may be set as the difference between that operating pressure and a pressure value that is 2.1 times that operating pressure.

In a case in which the first condition and the second condition are both
10 operating pressure rises, the second operating pressure rise is preferably higher than the first operating pressure rise, more preferably at least 20 kPa higher than the first operating pressure rise, and even more preferably at least 50 kPa higher than the first operating pressure rise.

[0054] The second operating time can be determined as appropriate depending
15 on the used device and the used concentration membrane or separation membrane and may, for example, be set as 240 hours.

In a case in which the first condition and the second condition are both operating times, the second operating time is preferably longer than the first operating time, more preferably at least 5 hours longer than the first operating
20 time, and even more preferably at least 10 hours longer than the first operating time.

[0055] The second predefined separation or concentration subject state can be determined as appropriate depending on the used device and the used concentration membrane or separation membrane. For example, the turbidity
25 of the subject may be taken periodically or continuously, and cleaning may be performed upon reaching a certain turbidity or higher so as to prevent blocking of the membrane by suspended matter.

The certain turbidity or higher may, for example, be set as 150 NTU or more. The turbidity in the second separation or concentration subject state is
30 preferably higher than the turbidity in the predefined separation or concentration subject state described above.

The turbidity can be measured by a method of causing the subject to flow through a turbidity meter.

Note that contaminants may be substances that adhere to the separation
35 membrane or the concentration membrane in the cleaning method of the present embodiment.

In a case in which the first condition and the second condition are both changes of the separation or concentration subject state, the second turbidity is preferably higher than the first turbidity, more preferably at least 20 NTU higher than the first turbidity, and even more preferably at least 50 NTU higher than the first turbidity.

[0056] The second permeability is normally set as a lower value than the first permeability of the separation membrane or the concentration membrane.

The second permeability may be set as a state at which 30 LMH/100 kPa is reached.

In a case in which the first condition and the second condition are both permeabilities, the second permeability is preferably lower than the first permeability, more preferably at least 10 LMH/100 kPa lower than the first permeability, and even more preferably at least 30 LMH/100 kPa lower than the first permeability.

[0057] {Cleaning device}

A cleaning device of the present embodiment includes at least a section where a separation membrane or a concentration membrane and a reduction cleaning liquid are brought into contact.

The cleaning device of the present embodiment is preferably a device that is used in the cleaning method of the present embodiment set forth above.

[0058] The section where the separation membrane or the concentration membrane and the reduction cleaning liquid are brought into contact may be a section where the separation membrane or the concentration membrane is installed in the device. For example, the section may be a case-type module such as previously described.

[0059] The cleaning device of the present embodiment may further include a tank in which the reduction cleaning liquid is stored, a pump that adjusts the flow rate of the reduction cleaning liquid, a pressure gauge, a flow meter, a heater that adjusts the temperature of the reduction cleaning liquid, a data logger that records a state, a limit element that prevents operating state abnormalities, a turbidity meter, etc.

[0060] The cleaning device of the present embodiment may be a device that includes a separation membrane or a concentration membrane.

For example, the cleaning device of the present embodiment may be the same device as a device that separates or concentrates a separation or concentration subject and may be a device in which the liquid flowing inside

thereof is switched from the separation or concentration subject to the
aforementioned reduction cleaning liquid. In this case, a plurality of channels
may be provided inside of the device, and switching may be performed between
a channel for when the separation or concentration subject is being separated
5 or concentrated and a channel for during the cleaning step.

The cleaning device is preferably a device that brings a reduction
cleaning liquid into contact with the separation membrane or the concentration
membrane at a pH of 7.0 or higher to clean the separation membrane or the
concentration membrane when there is satisfaction of any one of a situation in
10 which a predefined operating pressure has been reached, a situation in which a
predefined operating pressure rise has been reached, a situation in which a
predefined operating time has been reached, a situation in which a change to a
predefined separation or concentration subject state has occurred, and a
situation in which a decrease to a predefined separation or concentration
15 membrane permeability has occurred.

Moreover, the cleaning device is more preferably a device that brings
a reduction cleaning liquid into contact with the separation membrane or the
concentration membrane at a pH of 7.0 or higher to clean the separation
membrane or the concentration membrane when there is satisfaction of any one
20 of a situation in which the predefined operating pressure has been reached, a
situation in which the predefined operating pressure rise has been reached, a
situation in which the predefined operating time has been reached, a situation
in which a change to the predefined separation or concentration subject state
has occurred, and a situation in which a decrease to the predefined separation
25 or concentration membrane permeability has occurred and there is also
satisfaction of any one of a situation in which a predefined second operating
pressure has been reached, a situation in which a predefined second operating
pressure rise has been reached, a situation in which a predefined second
operating time has been reached, a situation in which a change to a predefined
30 second separation or concentration subject state has occurred, and a situation
in which a decrease to a predefined second separation or concentration
membrane permeability has occurred.

The cleaning device of the present embodiment may include a tank in
which the reduction cleaning liquid is stored, a pressure gauge that measures
35 operating pressure, a timer that measures operating time, an analyzer (for
example, a concentration meter) that analyzes a state (for example,

concentration) of a concentration subject, and an analyzer that analyzes permeability.

[0061] {Powder mixture}

A powder mixture of the present embodiment contains at least one or
5 more reductants selected from the group consisting of sodium hydrosulfite, thiourea dioxide, borohydrides, and sodium formaldehyde sulfoxylate and one or more alkalis selected from the group consisting of sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, and sodium bicarbonate. The powder mixture may be a mixture that is composed of only
10 the reductant and the alkali or may further contain other components.

The reductant may be any of the same reductants as previously described for the method of cleaning a separation membrane or a concentration membrane of the present embodiment set forth above, and preferable examples thereof are also the same.

15 The alkali may be any of the same alkalis as previously described for the method of cleaning a separation membrane or a concentration membrane of the present embodiment set forth above, and preferable examples thereof are also the same.

The mass proportion of the reductant relative to 100 mass% of the
20 powder mixture is preferably 10 mass% to 90 mass%, and more preferably 20 mass% to 80 mass%.

The mass proportion of the alkali relative to 100 mass% of the powder mixture is preferably 10 mass% to 90 mass%, and more preferably 20 mass% to 80 mass%.

25 The total mass proportion of the reductant and the alkali relative to 100 mass% of the powder mixture is preferably 80 mass% or more, more preferably 90 mass% or more, and even more preferably 95 mass% or more.

When 1 g of the powder mixture is mixed with 100 mL of water and is stirred at room temperature for 3 minutes until the powder has completely
30 disappeared, the pH at a temperature of 25°C is preferably 7.0 or higher, more preferably 9.0 to 14.0, and even more preferably 10.0 to 14.0.

The powder mixture is preferably a feedstock for a reduction cleaning liquid that is used for a separation membrane or a concentration membrane. The term feedstock for a reduction cleaning liquid means that when this powder
35 is dissolved in water with a concentration of 1% or more, it yields a reduction cleaning liquid having a pH of 7 or higher.

The powder mixture can be used to produce the reduction cleaning liquid in the method of cleaning a separation membrane or a concentration membrane of the present embodiment set forth above.

5 **[0062]** A method of producing a reduction cleaning liquid of the present embodiment is preferably a method in which the above-described reduction cleaning liquid having a pH of 7.0 or higher that is brought into contact with the separation membrane or the concentration membrane is produced from the powder mixture of the present embodiment set forth above.

10 The separation membrane or the concentration membrane may be the same as the separation membrane or the concentration membrane that was previously described for the method of cleaning a separation membrane or a concentration membrane of the present embodiment set forth above, and preferable examples thereof are also the same.

15 A reduction cleaning liquid obtained by the method of producing a reduction cleaning liquid of the present embodiment can be used as the reduction cleaning liquid in the method of cleaning a separation membrane or a concentration membrane of the present embodiment set forth above.

EXAMPLES

20 **[0063]** The following provides a more detailed description of the present disclosure based on examples. However, the present disclosure is not limited by these examples.

[0064] <Examples 1 to 3 and Comparative Examples 1 to 6>

25 With respect to a system in which treated liquid resulting from coagulation-sedimentation, activated carbon adsorption, and biological treatment (specifically, treatment including anaerobic biological treatment and aerobic biological treatment) of wastewater discharged from a dyeing factory is passed through a membrane module (UNA-620A produced by Asahi Kasei Corporation; spinning method: thermal induction; membrane material: PVDF; 30 pore diameter: 0.1 μm ; membrane area: 50 m^2) that performs filtration through MF membranes and then undergoes water treatment by a reverse osmosis membrane (RO) membrane, a UNA-620A that had been used in this system for approximately 1 year was subjected to cleaning recovery testing.

35 One UNA-620A was removed from the treatment system, the membrane module was disassembled, and hollow fiber membranes were cut out as roughly 30 cm in length. The sampling position was at a central portion of the 2 m

length and at an inner side of a bundle of 6,600 membranes. During this sequence of operations, the membranes were kept in a wet state to prevent drying out. Note that biopolymers originating from the aerobic biological treatment were adhered to the UNA-620A that had been removed from the treatment system.

Although biopolymers can be confirmed by various techniques, in the present disclosure, sugars and proteins of 104 Da or more that are measured using a liquid chromatography-organic carbon detection (LC-OCD) system were defined as biopolymers. Note that measurement was performed with reference to “Journal of the Japan Society of Civil Engineers G (Environment), Vol. 72, No. 7, III_535–III_541, 2016” and “Kimura, K., Tanaka, K., Watanabe, Y.: Confirmation of the correlation between membrane fouling in microfiltration and biopolymer concentrations in various Japanese surface water, Water Science and Technology: Water Supply, 15(2), 288–293, 2015”.

These hollow fiber membranes were trimmed to a length of 12 cm. With one end of the hollow fiber membranes in a sealed state, pure water was fed to inside of the hollow fiber membranes with a pressure of 100 kPa from the other end thereof, and, once the insides of the hollow fiber membranes had been purged with pure water, the weight of pure water that was discharged outside of the membranes in 1 minute was measured, and the water permeation flux was measured. The water temperature was also measured at this time. The water permeation flux is defined by the following formula.

Flux (LMH) = {(Total amount of water discharged from hollow fiber membranes (L/min)) × 60 (min) × Temperature correction of volume to 25°C}/Internal area of membranes (m²) ... Formula (2)

On the other hand, the water permeation flux of membranes prior to product shipping is measured and known for each lot. A water permeation retention ratio (%) is defined by the following formula. When the water permeation retention ratio is high, the membranes are judged to have their original water permeation ability.

Water permeation retention ratio (%) = (Flux of membranes in that state)/(Flux of unused membranes before shipping) × 100 ... Formula (3)

Measurement of water permeation flux in the present disclosure was performed by selecting 10 hollow fiber membranes, loading these hollow fiber membranes into a test tube having an internal capacity of approximately 35 mL, performing immersion cleaning for a specific time in a chemical liquid, and

making an evaluation based on the average water permeation flux of the 10 hollow fiber membranes.

The water permeation retention ratio determined from the average water permeation flux of 10 membranes in an uncleaned state after cutting out from the membrane module was of a very low level of 4.3%.

[0065] (Example 1)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, and water in a ratio of 96 mass% and was then loaded into a test tube. Ten membranes cut out from the above-described module were immersed in the reduction cleaning liquid and were left at rest at room temperature of 21°C to 22°C for 8 hours. The pH of the reduction cleaning liquid at room temperature as measured by a pH meter (HM-20P produced by DKK-TOA Corporation) was 12.9, and the redox potential of the reduction cleaning liquid at room temperature as measured by an ORP meter (RM-30P produced by DKK-TOA Corporation) was -795 mV. After 8 hours of immersion, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the ratio had recovered to 33.8%. The above described pH meter and ORP meter were also used to perform measurements in the following examples and comparative examples. Note that the pH meter was calibrated as appropriate, and the ORP meter was periodically confirmed to be operating normally through measurement of electromotive force using a standard solution and a reference electrode.

[0066] (Comparative Example 1)

A cleaning liquid was prepared in an amount of 50 g by mixing sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, and water in a ratio of 97.5 mass% and was then loaded into a test tube. Ten membranes cut out from the above-described module were immersed in the cleaning liquid and were left at rest at room temperature of 21°C to 22°C for 8 hours. This cleaning liquid had a pH of 13.3 and a redox potential of +310 mV at room temperature. After 8 hours of immersion, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the water permeation retention ratio was 7.8%, indicating a low cleaning effect compared to Example 1.

[0067] (Example 2)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, and water in a ratio of 96 mass%. The reduction cleaning liquid had a
5 pH of 13.0 and a redox potential of -800 mV at 40°C . The reduction cleaning liquid was loaded into a test tube, 10 membranes cut out from the above-described module were immersed in the reduction cleaning liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the inside of the test tube was also at 40°C , the
10 membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the water permeation retention ratio was 64.1%. Setting the temperature as 40°C was confirmed to further improve the water permeation retention ratio as compared to Example 1.

15 **[0068]** (Comparative Example 2)

A cleaning liquid was prepared in an amount of 50 g by mixing sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, and water in a ratio of 97.5 mass%. The cleaning liquid had a pH of 13.3 and a redox potential of $+320$ mV at 40°C . The cleaning liquid was loaded into a test
20 tube, 10 membranes cut out from the above-described module were immersed in the cleaning liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the inside of the test tube was also at 40°C , the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon
25 measurement of the water permeation retention ratio, the water permeation retention ratio was 12.7%. Little improvement of the water permeation retention ratio was observed even though the same immersion temperature of 40°C was adopted as compared to Example 2.

[0069] (Example 3)

30 A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G (anionic surfactant produced by Kotani Chemical Industry Co., Ltd.) in a ratio of 2 mass%, and water in a ratio of 94 mass%. The reduction cleaning liquid had a pH of 12.8 and a redox potential of -765 mV
35 at 40°C . The reduction cleaning liquid was loaded into a test tube, 10 membranes cut out from the above-described module were immersed in the

reduction cleaning liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the inside of the test tube was also at 40°C, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the water permeation retention ratio was 74.0%. The addition of a surfactant was confirmed to further improve the water permeation retention ratio compared to Example 2.

[0070] (Comparative Example 3)

A cleaning liquid was prepared in an amount of 50 g by mixing sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 95.5 mass%. The cleaning liquid had a pH of 13.2 and a redox potential of +280 mV at 40°C. This liquid was loaded into a test tube, 10 membranes cut out from the above-described module were immersed in the liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the inside of the test tube was also at 40°C, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the water permeation retention ratio was 38.6%. Although there was recovery of the water permeation retention ratio, the cleaning recovery effect was low compared to Example 3 and was insufficient.

[0071] (Comparative Example 4)

A cleaning liquid was prepared in an amount of 50 g by mixing a hydrosulfite in a ratio of 2.0 mass% and water in a ratio of 98.0 mass%. The cleaning liquid had a pH of 5.53 and a redox potential of -624 mV at 40°C. This liquid was loaded into a test tube, 10 membranes cut out from the above-described module were immersed in the liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the inside of the test tube was also at 40°C, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the water permeation retention ratio was 12.2% and the cleaning recovery effect was low.

[0072] (Comparative Example 5)

A cleaning liquid was prepared in an amount of 50 g by mixing caustic soda in a ratio of 2 mass% and water in a ratio of 98 mass%. The cleaning

liquid had a pH of 13.3 and a redox potential of -30 mV at 40°C . This liquid was loaded into a test tube, 10 membranes cut out from the above-described module were immersed in the liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the
5 inside of the test tube was also at 40°C , the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the water permeation retention ratio was 9.8% and the cleaning recovery effect was low and insufficient.

10 **[0073]** (Comparative Example 6)

A cleaning liquid was prepared in an amount of 50 g by mixing sodium sulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 94 mass%. The cleaning liquid had a pH of 13.3 and a redox potential of -125 mV at 40°C . This liquid was loaded
15 into a test tube, 10 membranes cut out from the above-described module were immersed in the liquid, and the test tube was loaded into a 40°C constant-temperature tank. Once 8 hours had passed after confirming that the inside of the test tube was also at 40°C , the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon
20 measurement of the water permeation retention ratio, the water permeation retention ratio was 12.9% and the cleaning recovery effect was low and insufficient.

[0074] [Table 1]

	Cleaning agent	Cleaning conditions	Water permeation retention ratio (%) (uncleaned water permeation retention ratio: 4.3%)
Example 1	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%	Room temperature, 8 hours	33.8
Example 2	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%	40°C, 8 hours	64.1
Example 3	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	40°C, 8 hours	74.0
Comparative Example 1	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%	Room temperature, 8 hours	7.8
Comparative Example 2	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%	40°C, 8 hours	12.7
Comparative Example 3	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	40°C, 8 hours	38.6
Comparative Example 4	Sodium hydrosulfite 2 mass%	40°C, 8 hours	12.2
Comparative Example 5	Caustic soda 2 mass%	40°C, 8 hours	9.8
Comparative Example 6	Sodium sulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	40°C, 8 hours	12.9

[0075] After cleaning, each of the membranes was freeze dried and was then measured by EDX under conditions of an accelerating voltage of 15 kV, a collection time of 60 seconds, and a measurement image width of 150 μm using an SU8000 produced by Hitachi High-Tech Corporation.

5 In the case of an unused membrane made of PVDF, only C and F are detected as illustrated in FIG. 2. This is based on a $-(\text{CH}_2-\text{CF}_2)_n-$ structure.

Comparative Examples 2 and 3 in which there was a low cleaning effect are illustrated in FIGS. 3 and 4. S, Cl, and Si peaks are observed in addition to those for C and F of the membrane material, and an O peak is also observed.
10 These are presumed to be elements due to adhered material caused by fouling.

In Examples 2 and 3, S, Cl, Si, and O peaks have disappeared as illustrated in FIGS. 5 and 6. Although the water permeation retention ratio recovered in Examples 2 and 3, the water permeation retention ratio did not recover to 100%, and some adhered material is thought to remain at the
15 membrane surface. However, the disappearance of an O peak is thought to indicate that O has been taken from adhered material through a reduction effect of the reduction cleaning liquid, thereby causing decomposition of the adhered material.

Changing the properties of adhered material through a reduction effect
20 of the reduction cleaning liquid in this manner is thought to facilitate stripping of the adhered material from a membrane. The cleaning effect is also thought to be further improved through heating in a temperature range of 1°C to 100°C, the presence of a surfactant, and so forth.

[0076] <Examples 4 to 8 and Comparative Example 7>

25 With respect to a system in which treated liquid resulting from coagulation-sedimentation and biological treatment (specifically, treatment including anaerobic biological treatment and aerobic biological treatment) of wastewater discharged from a liquid crystal factory is passed through a membrane module (UNA-620A produced by Asahi Kasei Corporation) that
30 performs filtration through MF membranes and then undergoes water treatment by a reverse osmosis membrane, a UNA-620A that had been used in this system for approximately 8 months was subjected to cleaning recovery testing.

Operations from removal of one UNA-620A from the treatment system, disassembly of the membrane module, and cutting out of hollow fiber
35 membranes onwards were performed by the same procedure as in Example 1 to measure the water permeation flux and the water permeation retention ratio.

The water permeation retention ratio of the membranes in an uncleaned state was 20.0%.

Note that biopolymers originating from the aerobic biological treatment were adhered to the UNA-620A that had been removed from the treatment system.

[0077] (Example 4)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 94 mass%. The reduction cleaning liquid had a pH of 13.0 and a redox potential of -790 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 20°C to 22°C for 2 hours. After 2 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, the ratio had recovered to 101.2%. The result that the water permeation retention ratio exceeded 100% may be taken to be due to variation compared to the water permeation flux of unused membranes of the same lot. This demonstrates that cleaning recovery could be completed in a short time.

[0078] (Example 5)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, ELEASE k1248 (non-ionic surfactant produced by METEL Corporation) in a ratio of 2 mass%, and water in a ratio of 94 mass%. The reduction cleaning liquid had a pH of 12.9 and a redox potential of -780 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 20°C to 22°C for 2 hours. After 2 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 100.5%. This demonstrates that through good selection of a surfactant, it is possible to complete cleaning recovery in a short time in the same manner as in Example 4.

[0079] (Example 6)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 0.1 mass%, caustic soda in a ratio of 0.1 mass%, EMILL 5G in a ratio of 0.1 mass%, and water in a ratio of 99.7 mass%. The reduction cleaning liquid had a pH of 11.9 and a redox potential of -761 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 20°C to 22°C for 2 hours. After 2 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 100.9%. This demonstrates that even when the concentration of the reduction cleaning liquid is reduced, the same cleaning effect is achieved in the case of this wastewater. **[0080]** (Example 7)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing thiourea dioxide in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, ELEASE k1248 in a ratio of 2 mass%, and water in a ratio of 94 mass%. The reduction cleaning liquid had a pH of 12.9 and a redox potential of -1,012 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 20°C to 22°C for 2 hours. After 2 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 101.5%. This demonstrates that a high cleaning effect is achieved not only with a hydrosulfite, but also with thiourea dioxide having reducing action.

Note that the absence of membrane deterioration after testing was confirmed.

[0081] (Example 8)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing thiourea dioxide in a ratio of 0.1 mass%, caustic soda in a ratio of 0.1 mass%, ELEASE k1248 in a ratio of 0.1 mass%, and water in a ratio of 99.7 mass%. The reduction cleaning liquid had a pH of 12.1 and a redox potential of -936 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described

module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 20°C to 22°C for 4 hours. After 4 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 99.7%.

[0082] (Comparative Example 7)

A cleaning liquid was prepared in an amount of 50 g by mixing sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2.0 mass%, and water in a ratio of 97.5 mass%. The cleaning liquid had a pH of 13.3 and a redox potential of +300 mV at room temperature. The cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the cleaning liquid, and the membranes were left at rest at a room temperature of 20°C to 22°C for 6 hours. Since color of the membrane surface indicated a state in which adhered material remained, the membranes were further cleaned with water and then immersed in a cleaning liquid of 1 mass% of citric acid and 99 mass% of water for 2 hours. After a total of 8 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 39.5%, but the cleaning recovery effect was insufficient.

[0083] [Table 2]

	Cleaning agent	Cleaning conditions	Water permeation retention ratio (%) (uncleaned water permeation retention ratio: 20.0%)
Example 4	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	Room temperature, 2 hours	101.2
Example 5	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, ELEASE k1248 2 mass%	Room temperature, 2 hours	100.5
Example 6	Sodium hydrosulfite 0.1 mass%, caustic soda 0.1 mass%, EMILL 5G 0.1 mass%	Room temperature, 2 hours	100.9
Example 7	Thiourea dioxide 2 mass%, caustic soda 2 mass%, ELEASE k1248 2 mass%	Room temperature, 2 hours	101.5
Example 8	Thiourea dioxide 0.1 mass%, caustic soda 0.1 mass%, ELEASE k1248 0.1 mass%	Room temperature, 4 hours	99.7
Comparative Example 7	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%	Room temperature, 6 hours	39.5
	Citric acid 1 mass%	Room temperature, 2 hours	

[0084] <Example 9 and Comparative Example 8>

A case-type module of 2 m in length in which 6,000 MF membranes made of polyethylene and having a pore diameter of 0.1 μm , an external diameter of 1.2 mm, and an internal diameter of 0.6 mm were bundled together and fixed at both ends was used for approximately 1 year of operation in a treatment process in which river water was pumped, was subjected to sedimentation-precipitation, and was then subjected to membrane filtration to obtain water for industrial use.

Operations from disassembly of this membrane module and cutting out of hollow fiber membranes onwards were performed by the same procedure as in Example 1 to measure the water permeation flux and the water permeation retention ratio.

The water permeation retention ratio of the membranes in an uncleaned state was 48.6%.

[0085] (Example 9)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, ELEASE k1248 in a ratio of 2 mass%, and water in a ratio of 94 mass%. The reduction cleaning liquid had a pH of 12.9 and a redox potential of -790 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 21°C to 23°C for 6 hours. After 6 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 90.2%.

In addition, a cleaning liquid was prepared in an amount of 50 g by mixing citric acid in a ratio of 1 mass% and water in a ratio of 99 mass%. The cleaning liquid was loaded into a test tube, the 10 membranes that had undergone the cleaning described above were immersed in the cleaning liquid, and the membranes were left at rest at a room temperature of 21°C to 23°C for 2 hours. Upon subsequent measurement of the water permeation flux after thorough rinsing, the water permeation retention ratio was 97.8%.

[0086] (Comparative Example 8)

A cleaning liquid was prepared in an amount of 50 g by mixing sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%,

RELEASE k1248 in a ratio of 2 mass%, and water in a ratio of 95.5 mass%. The cleaning liquid had a pH of 13.3 and a redox potential of +290 mV at room temperature. The cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the
5 cleaning liquid, and the membranes were left at rest at a room temperature of 21°C to 23°C for 6 hours. After 6 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 69.3%.

10 In addition, a cleaning liquid was prepared in an amount of 50 g by mixing citric acid in a ratio of 1 mass% and water in a ratio of 99 mass%. The cleaning liquid was loaded into a test tube, the 10 membranes that had undergone the cleaning described above were immersed in the cleaning liquid, and the membranes were left at rest at a room temperature of 21°C to 23°C for
15 2 hours. Upon subsequent measurement of the water permeation flux after thorough rinsing, the water permeation retention ratio was 88.4%.

[0087] [Table 3]

		Cleaning agent	Cleaning conditions	Water permeation retention ratio (%) (uncleaned water permeation retention ratio: 48.6%)
Example 9	First stage	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, ELEASE k1248 2 mass%	Room temperature, 6 hours	90.2
	Second stage	Citric acid 1 mass%	Room temperature, 2 hours	97.8
Comparative Example 8	First stage	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%, ELEASE k1248 2 mass%	Room temperature, 6 hours	69.3
	Second stage	Citric acid 1 mass%	Room temperature, 2 hours	88.4

[0088] <Examples 10 and 11 and Comparative Examples 9 and 10>

Four MF membrane modules (UNA-620A produced by Asahi Kasei Corporation; denoted as MF membrane in FIG. 7) that had been used for 8 months in a wastewater treatment process illustrated in FIG. 7 were cleaned by
5 methods described below. Note that biopolymers originating from aerobic biological treatment were adhered to the removed MF membranes.

[0089] (Example 10)

When a trans-membrane pressure difference of 20 kPa was applied to a first of the membrane modules and filtration of pure water was performed, the
10 water permeation retention ratio, which is the pure water permeation ability of the used membranes relative to the water permeation ability of the unused product prior to product shipping, was 46.3%. Note that the temperature during filtration of pure water was 23.9°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

15 The module was immersed in a warm water bath capable of temperature adjustment as illustrated in FIG. 8, and the temperature of the warm water bath was adjusted to 40°C. A reduction cleaning liquid was prepared in an amount of 50 kg by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of
20 94 mass%. The reduction cleaning liquid had a pH of 12.9 and a redox potential of -795 mV at 40°C. The reduction cleaning liquid was fed into the case from a side tube of the membrane module to achieve a full state. Immersion was performed for 8 hours in this state.

Thereafter, the reduction cleaning liquid was replaced by water and
25 thorough rinsing was performed. When a trans-membrane pressure difference of 20 kPa was subsequently applied to this membrane module and filtration of pure water was performed, the water permeation retention ratio, which is the water permeation ability after cleaning relative to the water permeation ability of the unused product prior to product shipping, was 95.4%, and thus the water
30 permeation retention ratio had recovered. Note that the temperature during filtration of pure water was 24.3°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

[0090] (Example 11)

When a trans-membrane pressure difference of 20 kPa was applied to a
35 second of the membrane modules and filtration of pure water was performed, the water permeation retention ratio was 44.2%. Note that the temperature

during filtration of pure water was 23.9°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

A reduction cleaning liquid was prepared in an amount of 100 kg by mixing sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 94 mass% in a tank capable of temperature adjustment as illustrated in FIG. 9. The reduction cleaning liquid had a pH of 13.0 and a redox potential of -800 mV at 40°C. A heater was installed inside of the tank, and the reduction cleaning liquid was held at 40°C. The reduction cleaning liquid was fed into the membrane module at a flow rate of 0.5 m³/hr, and the reduction cleaning liquid was caused to flow continuously for 8 hours at a surface of the membranes and also at an inner part and internal surface of the membranes through filtration.

Thereafter, the reduction cleaning liquid was replaced by water and thorough rinsing was performed. When a trans-membrane pressure difference of 20 kPa was subsequently applied to this membrane module and filtration of pure water was performed, the water permeation retention ratio was 99.5%, and thus the water permeation retention ratio had recovered. Note that the temperature during filtration of pure water was 24.6°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

[0091] (Comparative Example 9)

When a trans-membrane pressure difference of 20 kPa was applied to a third of the membrane modules and filtration of pure water was performed, the water permeation retention ratio was 47.6%. Note that the temperature during filtration of pure water was 23.9°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

The module was immersed in a warm water bath capable of temperature adjustment as illustrated in FIG. 8, and the temperature of the warm water bath was adjusted to 40°C. A cleaning liquid was prepared in an amount of 50 kg by mixing sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 95.5 mass%. The cleaning liquid had a pH of 13.3 and a redox potential of +310 mV at 40°C. The cleaning liquid was fed into the case from a side tube of the membrane module to achieve a full state. Immersion was performed for 8 hours in this state.

Thereafter, the cleaning liquid was replaced by water and thorough

rinsing was performed. When a trans-membrane pressure difference of 20 kPa was subsequently applied to this membrane module and filtration of pure water was performed, the water permeation retention ratio was 69.4%, and thus there was low recovery compared to Example 10 that differed only in terms of
5 cleaning liquid. Note that the temperature during filtration of pure water was 24.4°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

[0092] (Comparative Example 10)

When a trans-membrane pressure difference of 20 kPa was applied to a
10 fourth of the membrane modules and filtration of pure water was performed, the water permeation retention ratio was 48.4%. Note that the temperature during filtration of pure water was 23.9°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

A cleaning liquid was prepared in an amount of 100 kg by mixing
15 sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 95.5 mass% in a tank capable of temperature adjustment as illustrated in FIG. 9. The cleaning liquid had a pH of 13.3 and a redox potential of +310 mV at 40°C. A heater was installed inside of the tank, and the cleaning liquid was held at 40°C. The
20 cleaning liquid was fed into the membrane module at a flow rate of 0.5 m³/hr, and the cleaning liquid was caused to flow continuously for 8 hours at a surface of the membranes and also at an inner part and internal surface of the membranes through filtration.

Thereafter, the cleaning liquid was replaced by water and thorough
25 rinsing was performed. When a trans-membrane pressure difference of 20 kPa was subsequently applied to this membrane module and filtration of pure water was performed, the water permeation retention ratio was 78.3%, and thus there was low recovery compared to Example 11 that differed only in terms of cleaning liquid. Note that the temperature during filtration of pure water was
30 24.8°C and the water permeation retention ratio was calculated as a value converted for volume at 25°C.

[0093] [Table 4]

	Cleaning agent	Cleaning conditions	Water permeation retention ratio (%)
Example 10	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	Immersion, 8 hours	95.4
Example 11	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	Circulation, 8 hours	99.5
Comparative Example 9	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	Immersion, 8 hours	69.4
Comparative Example 10	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	Circulation, 8 hours	78.3

[0094] <Examples 12 and 13 and Comparative Examples 11 and 12>

Deterioration of membrane extension caused by cleaning liquids was investigated.

A PVDF membrane and a PE membrane were each immersed in a test
5 tube having a capacity of 35 mL for 10 days and were subsequently subjected
to measurement of tensile strength and tensile extension by a tensile test
machine with a chuck separation of 5 cm and a tensing rate of 200 mm/min.
The occurrence or absence of deterioration was investigated based on retention
ratios after 10 days and after 20 days relative to the strength and extension of
10 the membrane prior to immersion.

In actual membrane operation, filtration and cleaning are performed
repeatedly. Immersion in a chemical liquid for 20 days constitutes a method
representing membrane strength and extension after filtration and cleaning
have been performed for a period corresponding to the anticipated service life
15 of a membrane module.

[0095] (Example 12)

Sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2
mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 94 mass%
were mixed. The mixture had a pH of 12.8 and a redox potential of -790 mV
20 at 40°C. A PVDF membrane was immersed in a liquid of this reduction cleaning
liquid that was held at 40°C. The strength and extension after 10 days
respectively had retention ratios of 101.1% and 103.8% relative to an unused
membrane, and the strength and extension after 20 days respectively had
retention ratios of 102.1% and 108.8% relative to an unused membrane. Thus,
25 the absence of deterioration was confirmed.

[0096] (Example 13)

Sodium hydrosulfite in a ratio of 2 mass%, caustic soda in a ratio of 2
mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 94 mass%
were mixed. The mixture had a pH of 12.8 and a redox potential of -790 mV
30 at 40°C. A PE membrane was immersed in a liquid of this reduction cleaning
liquid that was held at 40°C. The strength and extension after 10 days
respectively had retention ratios of 99.2% and 102.5% relative to an unused
membrane, and the strength and extension after 20 days respectively had
retention ratios of 102.5% and 96.8% relative to an unused membrane. Thus,
35 the absence of deterioration was confirmed. A PE membrane has low
production cost since it is produced from a general-purpose resin, but is known

to also have low chemical resistance. The result that strength and extension do not deteriorate after 20 days of cleaning by the present technique indicates the potential for long-term use.

[0097] (Comparative Example 11)

5 Sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 95.5 mass% were mixed. The mixture had a pH of 13.0 and a redox potential of +310 mV at room temperature. A PVDF membrane was immersed in a liquid of this cleaning liquid that was held at 20°C to 23°C. The strength and extension after
10 10 days respectively had retention ratios of 95.0% and 84.0% relative to an unused membrane, and the strength and extension after 20 days respectively had retention ratios of 97.2% and 87.1% relative to an unused membrane. Thus, the occurrence of deterioration was confirmed as compared to the reduction cleaning liquid of Example 12.

15 **[0098]** (Comparative Example 12)

 Sodium hypochlorite in a ratio of 0.5 mass%, caustic soda in a ratio of 2 mass%, EMILL 5G in a ratio of 2 mass%, and water in a ratio of 95.5 mass% were mixed. The mixture had a pH of 13.0 and a redox potential of +310 mV at room temperature. A PE membrane was immersed in a liquid of this cleaning
20 liquid that was held at 20°C to 23°C. The strength and extension after 10 days respectively had retention ratios of 86.2% and 79.9% relative to an unused membrane, and the strength and extension after 20 days respectively had retention ratios of 85.6% and 66.9% relative to an unused membrane. Thus, the occurrence of deterioration was confirmed as compared to the reduction
25 cleaning liquid of Example 13.

[0099] [Table 5]

	PVDF membrane				PE membrane			
	Comparative Example 11		Example 12		Comparative Example 12		Example 13	
	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%		Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%		Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%		Sodium hydrosulfite 2 mass%, caustic soda 2 mass%, EMILL 5G 2 mass%	
Cleaning agent	Room temperature		40°C		Room temperature		40°C	
Cleaning conditions	Strength (N/mm)	Extension (%)	Strength (N/mm)	Extension (%)	Strength (N/mm)	Extension (%)	Strength (N/mm)	Extension (%)
0 hours	9.794	106	9.794	106	5.327	732	5.327	732
10 days	9.308 (95.0%)	89□ (84.0%)	9.90□ (101.1%)	110□ (103.8%)	4.592□ (86.2%)	585□ (79.9%)	5.286□ (99.2%)	750□ (102.5%)
20 days	9.520□ (97.2%)	92.3□ (87.1%)	10.00□ (102.1%)	115□ (108.8%)	4.560□ (85.6%)	490□ (66.9%)	5.460□ (102.5%)	709□ (96.8%)

[0100] In this manner, it was demonstrated that a cleaning liquid in which sodium hypochlorite is used causes deterioration to proceed as compared to when a reduction cleaning liquid is used even when conditions of 20°C to 23°C at which deterioration does not readily occur are adopted. Cleaning using a reduction cleaning liquid was confirmed to not only have a high cleaning effect, but also to not adversely affect mechanical characteristics of a membrane.

[0101] (Example 14)

A pencil module SLP-1053 produced by Asahi Kasei Corporation (UF membranes made of polysulfone; molecular weight cut off: 10,000; internal diameter: 1.4 mm; no. of membranes: 140; membrane area: 0.12 m²) was used to filter seasoning liquid (salt content: 5%) for dry-cured ham in order to perform disinfection and protein removal.

Filtration was performed until 29 L of feed liquid was concentrated 10 fold. The flux was initially 13 L/m²/hr but had decreased to 4 L/m²/hr after 40 hours once 10 fold concentration was complete.

The water permeation retention ratio of the membranes after concentration had decreased to 5%. When a reduction cleaning liquid of 2 mass% of a hydrosulfite, 2 mass% of caustic soda, and 96 mass% of water that had a temperature of 40°C and a pH of 13.1 and an ORP of -795 mV at 40°C was brought into contact with this module for 2 hours, the water permeation retention ratio was 84%, and sufficient recovery was possible.

[0102] (Comparative Example 13)

Concentration was performed with the same feed water, the same membrane module, and the same conditions as in Example 14. The flux was initially 13 L/m²/hr but had decreased to 4 L/m²/hr after 40 hours once 10 fold concentration was complete.

The water permeation retention ratio of the membranes after concentration had decreased to 6%. When a cleaning liquid of 0.5 weight% of sodium hypochlorite, 2 weight% of caustic soda, and 97.5 weight% of water that had a temperature of 40°C and a pH of 13.2 and a redox potential of +320 mV at 40°C was brought into contact with this module for 2 hours, the water permeation retention ratio was 61%, and cleaning recovery was insufficient.

[0103] [Table 6]

	Cleaning agent	Cleaning conditions	Water permeation retention ratio (%)
Example 14	Sodium hydrosulfite 2 mass%, caustic soda 2 mass%	40°C immersion, 2 hours	84
Comparative Example 13	Sodium hypochlorite 0.5 mass%, caustic soda 2 mass%	40°C immersion, 2 hours	61

[0104] <Example 15 and Comparative Example 14>

Operation was performed at a constant operating pressure using an RO element "FilmTec TW30-1812-100HR" produced by DuPont in which an aromatic polyamide membrane was used with wastewater (TOC: 10 mg/L to 20 mg/L; TDS: 5,000 mg/L to 8,000 mg/L) resulting from biological treatment (specifically, treatment including anaerobic biological treatment and aerobic biological treatment), sand filtration, and activated carbon adsorption of wastewater from a dyeing factory as feed water until the amount of permeated water of the membrane decreased to 40%.

The element was subsequently disassembled, and the membrane was cut out.

Biopolymers originating from the aerobic biological treatment were adhered to the membrane that had been cut out from the RO element.

[0105] (Example 15)

The disassembled fouled membrane was thoroughly rinsed with pure water, was subsequently loaded into a thin layer flow-type flat sheet membrane test cell C10-T (membrane area: 60 cm²) produced by Nitto Denko Corporation, and the water permeation retention ratio was measured.

The measurement was performed by pressurizing 300 ppm salt water with a liquid temperature of 25°C to 100 kPa and measuring the permeated weight per time of permeated water. In addition, the electrical conductivity of the permeated water was measured, and the salt removal ratio was also calculated.

Upon measurement of the fouled membrane, the water permeation retention ratio was 42% relative to a membrane after cleaning with respect to an unused membrane and the salt removal ratio was 98.3%.

Next, a cut out membrane was immersed for 8 hours in a reduction cleaning liquid (pH: 11.8; redox potential: -740 mV) containing 0.1 mass% of hydrosulfite, 0.1 mass% of caustic soda, and 0.1 mass% of EMILL 5G. Upon subsequent measurement in the same manner as above, the water permeability was 92% relative to a membrane after cleaning with respect to an unused membrane, the salt removal ratio was 97.9%, and thus water permeability had recovered without reduction of the removal ratio.

[0106] (Comparative Example 14)

A cut out membrane was immersed for 8 hours in 0.1 mass% caustic soda aqueous solution (pH: 11.9; redox potential: -28 mV). Upon subsequent

measurement in the same manner as above, the water permeability was 68% relative to a membrane after cleaning with respect to an unused membrane, the salt removal ratio was 97.8%, and thus although the removal ratio did not decrease, there was insufficient recovery of water permeability.

5 **[0107]** <Examples 16 and 17 and Comparative Example 15>

In a water treatment process in which recycling of water was performed by filtering sewage secondary treatment water as feed water using a membrane module UNA620A produced by Asahi Kasei Corporation and then performing RO treatment to obtain pure water, the effect of a cleaning liquid used in
10 maintenance cleaning was investigated.

Operating conditions were a feed water temperature of 20°C to 25°C, a flux during filtration of 50 LMH for 29 minutes, and a flux of 100 LMH for 1 minute of backwashing in which filtered water was passed through the membrane to the feed water side to perform cleaning. In addition, after 23
15 hours of operation in which filtration and backwashing were performed, 1 hour of maintenance cleaning in which a cleaning liquid was caused to flow from a filtrate side to a feed water side of the membranes at a flow rate of 3 L/min for 20 minutes and then settling was performed for a further 40 minutes was implemented.

20 **[0108]** (Example 16)

Upon 1 month of operation in which a reduction cleaning liquid that contained 0.1 mass% of a hydrosulfite and 400 mass ppm of caustic soda and had a pH of 7.4 and a redox potential of -685 mV was used as the cleaning liquid, the operating pressure changed from 40 kPa to 44 kPa, and thus it was
25 possible to continue operation without a sudden increase of pressure.

[0109] (Example 17)

Upon 1 month of operation in which a reduction cleaning liquid that contained 400 mass ppm of a hydrosulfite and 300 mass ppm of caustic soda and had a pH of 10.7 and a redox potential of -670 mV was used as the
30 reduction cleaning liquid, the operating pressure changed from 40 kPa to 46 kPa, and thus it was possible to continue operation without a sudden increase of pressure.

[0110] (Comparative Example 15)

Upon 1 month of operation in which a cleaning liquid that contained
35 600 mass ppm of sodium hypochlorite and had a pH of 12.0 and a redox potential of +505 mV was used as the cleaning liquid, the operating pressure

increased from 40 kPa to 110 kPa, indicating low effectiveness as maintenance cleaning.

[0111] <Examples 18 to 20 and Comparative Example 16>

With respect to a system in which treated liquid resulting from biological treatment (specifically, treatment including anaerobic biological treatment and aerobic biological treatment) of wastewater discharged from a semiconductor factory is passed through a membrane module (UNA-620A produced by Asahi Kasei Corporation) that performs filtration through MF membranes and then subjected to water treatment by a reverse osmosis membrane, a UNA-620A that had been used in this system for approximately 4 months was subjected to cleaning recovery testing.

Operations from removal of one UNA-620A from the treatment system, disassembly of the membrane module, and cutting out of hollow fiber membranes onwards were performed by the same procedure as in Example 1 to measure the water permeation flux and the water permeation retention ratio.

The water permeation retention ratio of the membranes in an uncleaned state was 47.3%.

Note that biopolymers originating from the aerobic biological treatment were adhered to the UNA-620A that had been removed from the treatment system.

[0112] (Example 18)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 1 mass%, caustic soda in a ratio of 1 mass%, and water in a ratio of 98 mass%. The reduction cleaning liquid had a pH of 13.0 and a redox potential of -821 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 21°C to 23°C for 2 hours. After 4 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 97.6%.

[0113] (Example 19)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 0.1 mass%, caustic soda in a ratio of 0.1 mass%, and water in a ratio of 99.8 mass%. The reduction cleaning liquid

had a pH of 12.0 and a redox potential of -789 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 21°C to 23°C for 2 hours. After 4 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 91.8%.

[0114] (Example 20)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hydrosulfite in a ratio of 0.05 mass%, caustic soda in a ratio of 0.05 mass%, and water in a ratio of 99.9 mass%. The reduction cleaning liquid had a pH of 11.8 and a redox potential of -771 mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 22°C to 24°C for 2 hours. After 4 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had recovered to 88.6%.

[0115] (Comparative Example 16)

A reduction cleaning liquid was prepared in an amount of 50 g by mixing sodium hypochlorite in a ratio of 0.1 mass%, caustic soda in a ratio of 0.1 mass%, and water in a ratio of 99.8 mass%. The reduction cleaning liquid had a pH of 12.2 and a redox potential of $+421$ mV at room temperature. The reduction cleaning liquid was loaded into a test tube, 10 membranes that had been cut out from the above-described module were immersed in the reduction cleaning liquid, and the membranes were left at rest at a room temperature of 22°C to 24°C for 2 hours. After 4 hours, the membranes were taken out of the test tube, and the water permeation flux was measured in the same manner. Upon measurement of the water permeation retention ratio, this ratio had only recovered to 67.2%.

The above demonstrates that although each of Examples 18 to 20 displayed a cleaning effect, a higher effect in terms of cleaning recovery was achieved with a higher pH and lower ORP.

[0116] [Table 7]

	Cleaning agent	Cleaning conditions	Water permeation retention ratio (%)
Example 18	Sodium hydrosulfite 1 mass%, caustic soda 1 mass%	Immersion, 8 hours	97.6
Example 19	Sodium hydrosulfite 0.1 mass%, caustic soda 0.1 mass%	Immersion, 8 hours	91.8
Example 20	Sodium hydrosulfite 0.05 mass%, caustic soda 0.05 mass%	Immersion, 8 hours	88.6
Comparative Example 16	Sodium hypochlorite 0.1 mass%, caustic soda 0.1 mass%	Immersion, 8 hours	67.2

[0117] <Example 21 and Comparative Example 17>

Operation was performed at a constant operating pressure using an RO element "CAP7-LD" produced by Nitto Denko Corporation with wastewater (TOC: 10 mg/L to 20 mg/L; TDS: 1,000 mg/L to 2,000 mg/L) resulting from
5 biological treatment (specifically, treatment including anaerobic biological treatment and aerobic biological treatment), sand filtration, and activated carbon adsorption of wastewater from a chemical factory as feed water until the amount of permeated water of the membrane decreased to 75%.

This element was subsequently disassembled, and the membrane was
10 cut out. Biopolymers originating from the aerobic biological treatment were adhered to the membrane removed from the RO element.

The amount of permeated water was determined using a Membrane Master C10-T (Nitto Denko Corporation). The amount of permeated water and the salt removal ratio were determined by the following calculations according
15 to an instruction manual accompanying the C10-T.

$$\text{Amount of permeated water} = 0.24 \times f \times V/T$$

Here, f is a temperature conversion coefficient of water, and V (mL) is an amount of water obtained by filtration in a specific time T (min).

The salt removal ratio was determined by:

20 Salt removal ratio = (Feed water electrical conductivity – Permeated water electrical conductivity)/Feed water electrical conductivity $\times$ 100.

[0118] (Example 21)

The disassembled fouled membrane was thoroughly rinsed with pure water, was subsequently loaded into a thin layer flow-type flat sheet membrane
25 test cell C10-T (membrane area: 60 cm²) produced by Nitto Denko Corporation, and the water permeation retention ratio was measured.

The measurement was performed by circulating 500 ppm salt water with a feed water liquid temperature of 25°C under pressurization of 700 kPa at 0.8 L/min and measuring the permeated weight per time of permeated water.
30 In addition, the electrical conductivity of permeated water was measured, and the salt removal ratio was calculated.

When a fouled membrane was cut out and the amount of permeated water and salt removal ratio were measured under the same conditions as with an uncleaned membrane, the water permeation retention ratio was 78.0%
35 relative to a membrane after cleaning with respect to an unused membrane and the salt removal ratio was 98.0%.

Next, the membrane was immersed in a reduction cleaning liquid (pH: 11.8; redox potential: -820 mV) containing 1 mass% of a hydrosulfite and 0.1 mass% of caustic soda for 16 hours and was subsequently rinsed using pure water. The amount of permeated water and the salt removal ratio were then
5 measured under the same conditions as the uncleaned membrane. The water temperature was 25°C. The water permeability was 97.9% relative to a membrane after cleaning with respect to an unused membrane, the salt removal ratio was 97.8%, and thus the water permeability recovered by 19.9% without reduction of the removal ratio.

10 **[0119]** (Comparative Example 17)

When a fouled membrane was cut out and the amount of permeated water and the electrical conductivity of filtered water were measured under the same conditions as in Example 21, the water permeation retention ratio was 81.2% relative to a membrane after cleaning with respect to an unused
15 membrane and the salt removal ratio was 97.8%.

Next, the membrane was immersed in 0.1 mass% caustic soda aqueous solution (pH: 11.9; redox potential: -35 mV) for 16 hours. When this membrane was subsequently measured in the same manner, the water permeability was 82.1% relative to a membrane after cleaning with respect to
20 an unused membrane, the salt removal ratio was 97.7%, and thus although the removal ratio did not decrease, the water permeability only recovered slightly by 0.9% and a sufficient cleaning recovery effect was not achieved.

[0120] [Table 8]

	Cleaning agent	Cleaning conditions	Permeability recovery (%)	Salt removal ratio (%)
Example 21	Sodium hydrosulfite 1 mass%, caustic soda 0.1 mass%	Immersion, 16 hours	19.9	97.6
Comparative Example 17	Caustic soda 0.1 mass%	Immersion, 16 hours	0.9	97.7

INDUSTRIAL APPLICABILITY

[0121] The method of cleaning a membrane according to the present disclosure can remove deposits adhering to a membrane surface, can restore permeability of the membrane, and can maintain filtration performance of the membrane.

CLAIMS

[Claim 1] A method of cleaning a separation membrane or a concentration membrane comprising a cleaning step of bringing a reduction cleaning liquid into contact with a separation membrane or a concentration membrane at a pH of 7.0 or higher.

[Claim 2] The method of cleaning a separation membrane or a concentration membrane according to claim 1, wherein the reduction cleaning liquid has a redox potential of -300 mV or less.

[Claim 3] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the reduction cleaning liquid has a pH of not lower than 7.0 and not higher than 14.0.

[Claim 4] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the reduction cleaning liquid has a redox potential of not less than $-1,200$ mV and not more than -500 mV.

[Claim 5] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein

the reduction cleaning liquid contains a reductant and an alkali,

the reductant is one or more selected from the group consisting of sodium hydrosulfite, thiourea dioxide, borohydrides, and sodium formaldehyde sulfoxylate, and

the alkali is one or more selected from the group consisting of sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, and sodium bicarbonate.

[Claim 6] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the cleaning step is performed at a temperature of 1°C to 100°C .

[Claim 7] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the reduction

cleaning liquid further contains a surfactant.

[Claim 8] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein

5 the separation membrane or the concentration membrane is a hollow fiber membrane or a flat sheet membrane,

the separation membrane or the concentration membrane is housed inside of a case,

10 a module having the separation membrane or the concentration membrane housed inside of the case is a case-type module, and

the cleaning step is a step of filling the reduction cleaning liquid into the case and bringing the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

15 [Claim 9] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein

the separation membrane or the concentration membrane is a hollow fiber membrane or a flat sheet membrane,

20 the separation membrane or the concentration membrane is housed inside of a case,

a module having the separation membrane or the concentration membrane housed inside of the case is a case-type module, and

25 the cleaning step is a step of causing the reduction cleaning liquid to pass through a surface and an inner part of the separation membrane or the concentration membrane and bringing the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

[Claim 10] The method of cleaning a separation membrane or a concentration membrane according to claim 8, wherein the case-type module
30 is an external pressure filtration type.

[Claim 11] The method of cleaning a separation membrane or a concentration membrane according to claim 9, wherein the case-type module
35 is an external pressure filtration type.

[Claim 12] The method of cleaning a separation membrane or a

concentration membrane according to claim 1 or 2, wherein the separation membrane or the concentration membrane is a membrane for separation or concentration in a wastewater treatment process, a water purification process, or a seawater desalination process.

5

[Claim 13] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the separation membrane or the concentration membrane is a UF membrane, an MF membrane, an RO membrane, an FO membrane, or an NF membrane.

10

[Claim 14] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the separation membrane or the concentration membrane is a membrane that contains one or more resins selected from the group consisting of PVDF, PE, PSF, PAN, PP, PTFE, ETFE, PA, and PES as a constituent component.

15

[Claim 15] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the cleaning step is a step of bringing one or more selected from the group consisting of an internal surface, an external surface, and an inner part of the separation membrane or the concentration membrane into contact with the reduction cleaning liquid.

20

[Claim 16] The method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, wherein the separation membrane or the concentration membrane is a membrane that has been used to separate or concentrate a solution after aerobic biological treatment.

25

[Claim 17] A cleaning method comprising a step of bringing a reduction cleaning liquid into contact with a separation membrane or a concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when, in operation of a device including the separation membrane or the concentration membrane, there is satisfaction of any one of a situation in which a predefined operating pressure has been reached, a situation in which a predefined operating pressure rise has been reached, a situation in which a predefined operating time has been reached, a

30

35

situation in which a change to a predefined separation or concentration subject state has occurred, and a situation in which a decrease to a predefined separation or concentration membrane permeability has occurred.

5 [Claim 18] The cleaning method according to claim 17, comprising a step of bringing a reduction cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when there is satisfaction of any one of a situation in which the predefined operating pressure has been
10 reached, a situation in which the predefined operating pressure rise has been reached, a situation in which the predefined operating time has been reached, a situation in which a change to the predefined separation or concentration subject state has occurred, and a situation in which a decrease to the predefined separation or concentration membrane permeability has occurred and there is
15 also satisfaction of any one of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating pressure rise has been reached, a situation in which a predefined second operating time has been reached, a situation in which a change to a predefined second separation or concentration subject state has occurred, and
20 a situation in which a decrease to a predefined second separation or concentration membrane permeability has occurred.

[Claim 19] A cleaning device used in the method of cleaning a separation membrane or a concentration membrane according to claim 1 or 2, comprising
25 a section where the separation membrane or the concentration membrane and the reduction cleaning liquid are brought into contact.

[Claim 20] A device comprising a separation membrane or a concentration membrane, wherein the device brings a reduction cleaning liquid into contact
30 with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation membrane or the concentration membrane when there is satisfaction of any one of a situation in which a predefined operating pressure has been reached, a situation in which a predefined operating pressure rise has been reached, a situation in which a predefined operating time has been
35 reached, a situation in which a change to a predefined separation or concentration subject state has occurred, and a situation in which a decrease to

a predefined separation or concentration membrane permeability has occurred.

[Claim 21] The device according to claim 20, wherein the device brings a reduction cleaning liquid into contact with the separation membrane or the concentration membrane at a pH of 7.0 or higher to clean the separation
5 membrane or the concentration membrane when there is satisfaction of any one of a situation in which the predefined operating pressure has been reached, a situation in which the predefined operating pressure rise has been reached, a situation in which the predefined operating time has been reached, a situation
10 in which a change to the predefined separation or concentration subject state has occurred, and a situation in which a decrease to the predefined separation or concentration membrane permeability has occurred and there is also satisfaction of any one of a situation in which a predefined second operating pressure has been reached, a situation in which a predefined second operating
15 pressure rise has been reached, a situation in which a predefined second operating time has been reached, a situation in which a change to a predefined second separation or concentration subject state has occurred, and a situation in which a decrease to a predefined second separation or concentration membrane permeability has occurred.

20