

SPECIFICATION

Title of Invention

Combined chlorine agent and production and use thereof

Technical Field

[0001]

The present invention relates to a combined chlorine agent used suitably for a slime control agent of a reverse osmosis membrane (in the following sometimes called as "RO membrane") and methods of production and use thereof. More specifically, the present invention relates to a combined chlorine agent having a low concentration of free chlorine and a high concentration of combined chlorine, to a method of efficient production thereof and a method of chlorine treatment using the combined chlorine agent.

Technical Background

[0002]

Since a RO membrane reveals a high rejection rate of solute, clear permeate obtained by a RO membrane treatment has a superior water quality and can be reused effectively for a variety of purposes. If, however, water to be treated contains contaminants such as suspended solids and organic substances which foul the RO membrane, there is a problem wherein the RO membrane is contaminated by these contaminants causing declines of flux and rejection rate as the treatment lasts.

[0003]

In water treatment using a RO membrane, a method continuing a stable operation by averting obstruction such as decline of flux and increase of operational pressure in a RO membrane apparatus is performed by adopting pretreatment (including coagulation, solid-liquid separation and active carbon treatment) to clarify feed water to the RO membrane, wherein, in order to prevent fouling of the RO membrane and to obtain a high treatment efficiency, the feed water to the RO membrane apparatus is evaluated by a Fouling Index (FI) ruled in JIS K3802, or Silt Density Index (SDI) ruled in ASTM D4189, and the pretreatment is carried out wherein FI or SDI falls in a predetermined value or lower, for instance, FI or SDI becomes 3 - 4 or lower.

[0004]

In cooling water circulation system, a part of water evaporates when cooling water used for cooling a heat source is cooled in a cooling tower, whereby contaminants such as suspended solids and organic substances are condensed. Further, to the cooling water, bacteria causing slime formation mix from outer side and slimes formed in the cooling tower mix by exfoliating, so that sterilization for slime control becomes necessary. Since, even if contaminants such as suspended solids and organic substances have been removed, bacteria contained in the water to be treated proliferate on the surface of RO membrane to decrease flux of permeate, sterilization of water to be treated is performed by adding a sterilizer to prevent fouling of membrane by proliferation of bacteria.

[0005]

As a sterilizer for general water systems, a free chlorine agent such as chlorine and sodium hypochlorite is widely used which causes, as an oxidizing agent, deterioration of RO membrane

and decline of efficiency. In order to ease oxidizing effect, Patent Document 1 (JP H01-104310A) proposes formation of chloramine by adding ammonium ion after sterilization by a free chlorine agent. However, Patent Document 1 does not disclose application to water to be treated containing contaminant in detail, for instance, when and how to apply.

[0006]

Patent document 2 (JP2006-263510A) teaches a slime control agent for membrane separation which comprises a combined chlorine agent comprising an oxidizing agent based on chlorine and a sulfamic compound. Patent document 2 also teaches that free chlorine is contained in specific ratio to the above combined chlorine agent added into water to be treated, and that there is a correlation similar to equilibrium. In order to obtain sterilizing effect, the above combined chlorine agent is to be used in a concentration wherein free chlorine is detected in the water to be treated, while the combined chlorine agent is used in a concentration wherein free chlorine concentration is 2 - 6 mg/L and total chlorine concentration is 20 - 60 mg/L in the Examples.

[0007]

Since there are problems that a RO membrane, especially a RO membrane composed of high molecular weight membrane having a nitrogen-containing group such as polyamide and aramid is easily damaged by free chlorine deteriorating membrane separation efficiency such as rejection rate and removing rate, it is important to perform RO membrane treatment in a condition wherein free chlorine is not contained. For this, Patent document 3 (JP H09-57067A) proposes to carry out RO membrane treatment after sterilizing by free chlorine agent and then eliminating the sterilizing agent by adding reducing agent such as sodium bisulfite.

In Patent document 3, copper concentration is restricted because effect of elimination of sterilizing agent by addition of reducing agent is insufficient. It is suggested that elimination of free chlorine after sterilization by free chlorine agent is necessary.

[0008]

Since, as above, a RO membrane, especially a RO membrane composed of high molecular weight membrane having a nitrogen-containing group such as polyamide and aramid is required to be used in a water system containing no free chlorine, residual chlorine should be removed from a feed water sterilized with a chlorine agent before supplying to a RO membrane. If, however, the feed water is supplied to a RO membrane after residual chlorine has been removed, slimes will be formed as the treatment lasts to cause deterioration of membrane performance. In order to avert these problems, a combined chlorine agent as shown in Patent document 2 can be added in a free chlorine concentration of 0.1 m/L or lower. This method may be possible in the case that the combined chlorine agent is prepared on the spot to be added. However, in the case that a combined chlorine agent prepared in a factory is added, after storage and transportation, on the spot so as to be diluted to a free chlorine concentration of 0.1 m/L or lower, there occurs a problem that combined chlorine (total chlorine) concentration becomes low to decrease slime prevention effect. Accordingly, there is a demand for a combined chlorine agent having a low concentration of free chlorine and a high concentration of combined chlorine.

Prior Technical Document

[Patent Document]

[0009]

Patent document 1: JP H01-104310A

Patent document 2: JP2006-263510A

Patent document 3: JP H09-57067A

Summary of Invention

[Subject to be solved by Invention]

[0010]

An object of the present invention is to provide, in order to solve the above prior problem, a combined chlorine agent having a low concentration of free chlorine and a high concentration of combined chlorine whereby combined chlorine concentration of water can be heightened when added to water systems at a low concentration of free chlorine. Another object of the present invention is to provide a method for producing the combined chlorine agent efficiently. A further object of the present invention is to provide a method of chlorine treatment under condition of a low free chlorine concentration.

Means to solve subject

[0011]

The present invention consists in the following combined chlorine agent, method of production thereof and method of chlorine treatment;

(1) A combined chlorine agent consisting of an aqueous agent which comprises alkali consisting of alkali metal hydroxide, sulfamic acid, and oxidizing agent based on chlorine,

wherein the composition ratio of the oxidizing agent based

on chlorine to the sulfamic acid is in the range from 0.45 to 0.6 by Cl / N (mole ratio),

the composition ratio of the oxidizing agent based on chlorine to alkali is in the range from 0.3 to 0.4 by Cl / alkali metal (mole ratio), and

free chlorine concentration in the aqueous agent is 2 % by weight or lower of total chlorine concentration.

(2) The combined chlorine agent according to the above (1), wherein the combined chlorine agent is used for slime control agent of a reverse osmosis membrane.

(3) A method of producing the combined chlorine agent according to the above (1) or (2), comprising

adding sulfamic acid to an aqueous solution of alkali consisting of alkali metal hydroxide to dissolve,

adding oxidizing agent based on chlorine to the obtained sulfamic acid - alkali aqueous mixture, and

mixing the finally obtained aqueous mixture to form an aqueous solution agent.

(4) The method of producing the combined chlorine agent according to the above (3), wherein the aqueous solution of alkali has a water content of 50 - 65 % by weight.

(5) A method of chlorine treatment, comprising

adding the combined chlorine agent according to the above (1) to a water system so that free chlorine concentration is 0.1 mg/L or lower.

(6) A method of chlorine treatment, comprising

adding the combined chlorine agent according to the above (1) to a feed water system to a reverse osmosis membrane so that free chlorine concentration is 0.1 mg/L or lower.

[0012]

According to the present invention, free chlorine, combined chlorine, and total chlorine concentration are given in JIS K 0400-33-10:1999 and measured as Cl_2 concentration by DPD method using N,N-diethyle-1,4-phenylenediamine. Free chlorine is ruled as chlorine residing in a form of hypochlorous acid, hypochlorite ion or dissolved chlorine. Combined chlorine is ruled as chlorine residing in a form of chloramine or organic chloramine which is measured by the DPD method but excluded from the free chlorine. Total chlorine is ruled as chlorine in forms of free chlorine and/or combined chlorine.

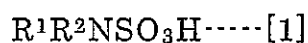
[0013]

A combined chlorine agent is an agent forming the above combined chlorine. The combined chlorine agent according to the present invention is an aqueous agent comprising alkali consisting of alkali metal hydroxide, sulfamic acid, and oxidizing agent based on chlorine. In the combined chlorine agent of the present invention, the composition ratio of the oxidizing agent based on chlorine to the sulfamic acid in the aqueous agent is in the range from 0.45 to 0.6, preferably 0.45 - 0.55 by Cl / N (mole ratio), the composition ratio of the oxidizing agent based on chlorine to alkali in the aqueous agent is in the range from 0.3 to 0.4, preferably 0.30 - 0.36 by $\text{Cl} / \text{alkali metal}$ (mole ratio), and free chlorine concentration in the aqueous agent is 2 % by weight or lower of total chlorine concentration. The aqueous solution agent is preferably of pH 13 or more and the composition ratio of sulfamic acid to alkali in the aqueous solution agent is in the range from 0.5 to 0.7 by $\text{N} / \text{alkali metal}$ (mole ratio). The above Cl / N (mole ratio) corresponds to the ratio of Cl_2 mole number of the oxidizing agent measured according to JIS K 0400-33-10:1999 to mole number of sulfamic acid composed of N. The above N / alkali

metal (mole ratio) corresponds to the ratio of the above mole number of sulfamic acid to mole number of alkali metal formed by alkali metal hydroxide.

[0014]

Sulfamic acid to form the combined chlorine agent is amidosulfuric acid represented by



wherein R^1, R^2 denote each H or hydrocarbon group having carbon number of 1-6 independently. Preferable sulfamic acid is the one in narrow sense in which R^1, R^2 denote each H, while N-methyl sulfamic acid, N,N-dimethyl sulfamic acid, N-phenyl sulfamic acid, and so on may be used. Sulfamic acid may be used in the state of free acid (in powder) or sulfamate such as alkali metal salt including sodium salt and potassium salt.

[0015]

Alkali for composing a combined chlorine agent consists of alkali metal hydroxide such as sodium hydroxide and potassium hydroxide. An oxidizing agent based on chlorine includes hypochlorous acid, chlorous acid and water soluble salt thereof such as alkali metal salt thereof. These are preferably of no content of sodium chloride. By controlling sodium chloride content in the aqueous agent at 50,000 mg/L or lower, precipitation of salt is prevented and stability of a halogenated oxidizing agent becomes increased.

[0016]

The combined chlorine agent is produced by a method wherein sulfamic acid is added to an aqueous solution of alkali consisting of alkali metal hydroxide to dissolve, then an oxidizing agent based on chlorine is added to the obtained sulfamic acid - alkali aqueous mixture, and the finally obtained aqueous mixture

is mixed to form an aqueous solution agent. The aqueous solution of alkali preferably contains 50 - 65 % by weight of water. Alkali consists of alkali metal hydroxide such as sodium hydroxide and potassium hydroxide which maintains solubility when the aqueous solution of the combined chlorine agent has formed.

[0017]

Sulfamic acid may be added in a form of sulfamate. Usable sulfamate includes sodium sulfamate, potassium sulfamate, and ammonium sulfamate which are soluble when the aqueous solution of the combined chlorine agent has formed. Sulfamic acid is added in order that sulfamic acid concentration in the aqueous solution agent becomes to be the above concentration. Amount of sulfamic acid to be added is preferably the amount wherein composition ratio of sulfamic acid to alkali is in the range from 0.5 to 0.7 by N / alkali metal (mole ratio). Sulfamic acid may be added in a form of powder or aqueous solution of sulfamic acid or sulfamate. In the case using sulfamate, amount of alkali metal contained in sulfamate is calculated as alkali. In the case using an aqueous solution, amount of water contained in the aqueous solution is added as water in the aqueous solution of alkali.

[0018]

Oxidizing agent based on chlorine is preferably hypochlorous acid or hypochlorite which is preferably added as an aqueous solution having available chlorine (Cl_2) concentration of 5 - 20 % by weight, preferably 10 - 15 % by weight. Additive amount of oxidizing agent based on chlorine is decided in order that combined chlorine concentration in the aqueous solution agent becomes the above concentration as available chlorine (Cl_2) concentration, and that composition ratio of oxidizing agent based on chlorine to sulfamic compound by Cl / N (mole ratio) becomes the

above ratio, whereby a combined chlorine agent of aqueous solution agent superior in reactivity, stability, handling and scentlessness of chlorine is produced efficiently without foaming and emitting chlorine odor. Here, oxidizing agent based on chlorine is preferably added and mixed gradually.

[0019]

The combined chlorine agent according to the present invention as produced above is used by adding to water system for chlorine treatment. The agent has low free chlorine concentration and high combined chlorine concentration, so that combined chlorine concentration of water system to which the agent has been added can be heightened even when added at a low free chlorine concentration. Since chlorine in the combined chlorine agent is in a form decided by equilibrium between free chlorine and combined chlorine (total chlorine), it is presumed that, even in case of low free chlorine concentration, chlorine latently stored in a form of combined chlorine is released gradually to give an effect by a chlorine agent such as sterilization. Therefore, the water system added with the combined chlorine agent is laid in a sterilization-active state so that slime forming is prevented. The combined chlorine agent can be added to water system at a free chlorine concentration of 0.1 mg/L or lower to perform chlorine treatment. In this case, total chlorine concentration may be 1 - 50 mg/L.

[0020]

The combined chlorine agent according to the present invention is suitably used for slime control agent for RO membrane. RO membrane is a permeation membrane to separate and remove solutes such as salts, organic matters and so on from water to be treated by reverse osmosis. RO membranes generally used for

reverse osmosis membrane treatment are proper object of the present invention. For the material of the RO membrane, the present invention is especially effective to a polymer membrane having nitrogen-containing group, such as polyamide (especially aromatic polyamide of low tolerance to chlorine), polyurea, and polypiperazine amide, while other RO membranes based on such as cellulose acetate may be applicable. The RO membrane may have a structure of module such as spiral type, hollow fiber type, tubular type, and flat membrane type.

[0021]

The objective water to be treated by RO membrane treatment according to the present invention may be water to be treated containing contaminative substances. Such water to be treated is subjected to pretreatment for removing contaminative substances under presence of free chlorine to cancel contaminative power to RO membrane and to control free chlorine concentration to be 0.1 mg/L or lower, whereby RO membrane treatment can be performed efficiently while preventing contamination and deterioration of RO membrane. In order to control the free chlorine concentration of pretreated water being the above value, a reducing agent may be added to the pretreated water. According to the present invention, such water to be treated for RO membrane is subjected to chlorine treatment by adding the combined chlorine agent to control the free chlorine concentration to be 0.1 mg/L or lower, whereby slime control of RO membrane can be performed. Here, total chlorine concentration may be 1 – 50 mg/L.

[Effect of Invention]

[0022]

According to the present invention, a combined chlorine

agent having a low concentration of free chlorine and a high concentration of combined chlorine can be obtained, whereby combined chlorine concentration can be heightened even if added at a low free chlorine concentration.

According to the method for producing the combined chlorine agent of the present invention, such combined chlorine agent can be produced efficiently.

According to the method of chlorine treatment of the present invention, chlorine treatment under condition of a low free chlorine concentration can be performed by adding the above combined chlorine agent. In the case that the combined chlorine agent is used for slime control agent of RO membrane, slime control is performed without damage of RO membrane whereby RO membrane treatment can be carried out efficiently.

Description of Drawings

[0023]

Fig. 1 is a graph showing correlation between Cl/N (mol ratio) and free chlorine concentration in Examples 1 - 3 and Comparative Examples 1 - 3.

Fig. 2 is a graph showing variations of permeate and pressure drop in Example 4.

Fig. 3 is a graph showing variation of salt rejection in Example 4.

Fig. 4 is a graph showing variation of permeate and pressure drop in Comparative Example 9.

Fig. 5 is a graph showing variation of salt rejection in Comparative Example 9.

Fig. 6 is a graph showing variation of permeate and pressure

drop in Comparative Example 10.

Fig. 7 is a graph showing variation of salt rejection in Comparative Example 10.

[Embodiment of Invention]

[0024]

Below, the present invention is explained by way of Examples and Comparative Examples wherein % denotes "% by weight" and part denotes "part by weight" unless specific indication is given.

[Examples]

[0025]

[Examples 1-3]:

To pure water in amount shown for each Example in Table 1, sodium hydroxide was added to dissolve, then sulfamic acid (powdery sulfamic acid wherein R^1, R^2 in the above formula 1 denote each H) was added to dissolve, and then sodium hypochlorite in amount shown for each Example in Table 1 was added to dissolve whereby combined chlorine agent of aqueous solution agent of each Example was produced. Characteristics, free chlorine concentration and total chlorine concentration of the obtained aqueous solution agents were shown in Table 1. In Tables 1 - 4, NaOH (Na mol/L), N (mol/L) and available chlorine (mol/L) were shown as value each calculated as specific gravity of the solution is 1.3.

[0026]

[Table 1]

	Example 1	Example 2	Example 3
Main component	Comb. Cl agent	Comb. Cl agent	Comb. Cl agent
Pure water (part)	15.5	13.2	8.6
48% NaOH (part)	19.5	20.8	23.4
Sulfamic acid (part)	15.0	16.0	18.0
12%(Cl ₂) NaClO (part)	50.0	50.0	50.0
Total (part)	100	100	100
NaOH(Na mol/L)	3.043	3.246	3.651
N(mol/L)	2.009	2.143	2.411
Available Cl(mol/L)	1.099	1.099	1.099
N/Na(mol ratio)	0.66	0.66	0.66
Cl/N(mol ratio)	0.55	0.51	0.46
Cl/Na(mol ratio)	0.36	0.34	0.30
pH (when prepared)	pH>13	pH>13	pH>13
Free Cl(when prepared) (mg/L)	<1000	<1000	<1000
Total Cl(when prepared) (%)	6.9	6.9	6.9
Appearance (when prepared)	Good	Good	Good
pH(after 7 days storage at 40°C)	pH>13	pH>13	pH>13
Free Cl(after 7 days storage at 40°C) (mg/L)	930	920	940
Total Cl(after 7 days storage at 40 °C) (%)	6.9	6.9	6.9
Appearance (after 7 days storage at 40°C)	Good	Good	Good
Appearance (after 7 days storage at -5°C)	Good	Good	Good

[0027]

[Comparative Examples 1-3]:

Examples 1-3 were pursued except that composition of each component was changed as described in Table 2. Results of Comparative Examples 1-3 were shown in Table 2. In Comparative Example 1, two parts of benzotriazole were added as another component to sum total amount of 100 parts which was shown with *1 in Table 2.

[0028]

[Table 2]

	Comp. Example 1	Comp. Example 2	Comp. Example 3
Main component	Comb. Cl agent	Comb. Cl agent	Comb. Cl agent
Pure water (part)	6.7	12.4	6.6
48% NaOH (part)	19.3	15.6	18.9
Sulfamic acid (part)	12.0	12.0	14.5
12%(Cl ₂) NaClO (part)	60.0	60.0	60.0
Total (part)	100 *1	100	100
NaOH(Na mol/L)	3.012	2.434	2.949
N(mol/L)	1.607	1.607	1.942
Available Cl(mol/L)	1.319	1.319	1.319
N/Na(mol ratio)	0.53	0.66	0.66
Cl/N(mol ratio)	0.82	0.82	0.68
Cl/Na(mol ratio)	0.44	0.54	0.45
pH (when prepared)	pH>13	pH>13	pH>13
Free Cl(when prepared) (mg/L)	6000	6000	2000
Total Cl(when prepared) (%)	7.7	7.7	7.7
Appearance (when prepared)	Good	Good	Good
pH(after 7 days storage at 40 °C)	pH>13	pH>13	pH>13
Free Cl(after 7 days storage at 40 °C) (mg/L)	8000	-	-
Total Cl(after 7 days storage at 40 °C) (%)	7.1	-	-
Appearance (after 7 days storage at 40 °C)	Good	Good	Good
Appearance (after 7 days storage at -5 °C)	Good	Good	Good

[0029]

[Comparative Examples 4-6]:

Examples 1-3 were pursued except that composition of each component was changed as described in Table 3, wherein sulfamic acid was not able to dissolve into the aqueous solution of pure water added with sodium hydroxide (shown as "Deposit"). Results of Comparative Examples 4-6 were shown in Table 3.

[0030]

[Table 3]

	Comp. Example 4	Comp. Example 5	Comp. Example 6
Main component	Comb. Cl agent	Comb. Cl agent	Comb. Cl agent
Pure water (part)	6.6	4.0	6.7
48% NaOH (part)	24.4	26.0	27.3
Sulfamic acid (part)	19.0	20.0	21.0
12%(Cl ₂) NaClO (part)	50.0	50.0	45.0
Total (part)	100	100	100
NaOH(Na mol/L)	3.808	4.057	4.260
N(mol/L)	2.545	2.678	2.812
Available Cl(mol/L)	1.099	1.099	0.989
N/Na(mol ratio)	0.67	0.66	0.66
Cl/N(mol ratio)	0.43	0.41	0.35
Cl/Na(mol ratio)	0.29	0.27	0.23
pH (when prepared)	-	-	-
Free Cl(when prepared) (mg/L)	-	-	-
Total Cl(when prepared) (%)	-	-	-
Appearance(when prepared)	Deposit	Deposit	Deposit
pH(after 7 days storage at 40 °C)	-	-	-
Free Cl(after 7 days storage at 40 °C) (mg/L)	-	-	-
Total Cl(after 7 days storage at 40 °C) (%)	-	-	-
Appearance (after 7 days storage at 40 °C)	-	-	-
Appearance (after 7 days storage at -5 °C)	-	-	-

[0031]

[Comparative Examples 7-8]:

Examples 1-3 were pursued except that composition of each component was changed as described in Table 4, wherein sulfamic acid was not able to dissolve into the aqueous solution of pure water added with sodium hydroxide. Results of Comparative Examples 7-8 were shown in Table 4.

[0032]

[Table 4]

	Comp. Example 7	Comp. Example 8
Main component	Comb. Cl agent	Comb. Cl agent
Pure water (part)	13.6	9.0
48% NaOH (part)	23.4	26.0
Sulfamic acid (part)	18.0	20.0
12%(Cl ₂) NaClO (part)	45.0	45.0
Total (part)	100	100
NaOH(Na mol/L)	3.651	4.057
N(mol/L)	2.411	2.678
Available Cl(mol/L)	0.989	0.989
N/Na(mol ratio)	0.66	0.66
Cl/N(mol ratio)	0.41	0.37
Cl/Na(mol ratio)	0.27	0.24
pH (when prepared)	-	-
Free Cl(when prepared) (mg/L)	-	-
Total Cl(when prepared) (%)	-	-
Appearance (when prepared)	Deposit	Deposit
pH(after 7 days storage at 40 °C)	-	-
Free Cl(after 7 days storage at 40 °C) (mg/L)	-	-
Total Cl(after 7 days storage at 40 °C) (%)	-	-
Appearance(after 7 days storage at 40 °C)	-	-
Appearance(after 7 days storage at -5 °C)	-	-

[0033]

In Examples 1-3 and Comparative Examples 1-3, correlation between Free chlorine concentration/Sulfamic acid (mol ratio), namely Cl/N (mol ratio) and Free chlorine concentration is shown in Fig. 1, wherein free chlorine concentrations in Comparative Examples 1-3 were calculated so that the total chlorine concentration were 6.9 % as same as Examples 1-3.

[0034]

The above result shows that, in Examples 1-3, free chlorine concentration in the aqueous agent is 1000 mg/L or lower which falls in 2 % by weight or lower of total chlorine concentration and that in Comparative Examples 1-3, free chlorine concentration in the aqueous agent is higher than 1000 mg/L which is higher than 2 % by weight of total chlorine concentration. Although total chlorine concentration in Examples 1-3 is lower than in Comparative Examples 1-3, the difference of total chlorine concentration is smaller than the difference of free chlorine concentration. It is also shown that, in Comparative Examples 4-8, an aqueous agent can not be produced because deposit occurs.

[0035]

[Examples 4]:

Cooling water discharged from a cooling tower was added with a combined chlorine agent and subjected to coagulation treatment, filtration and active carbon treatment to obtain a pretreated water having total chlorine concentration of 5 mg/L and free chlorine concentration of 0.5 mg/L. The pretreated water was added with 10% by weight of aqueous solution of sodium bisulfite was added at sodium bisulfite concentration of 15 mg/L to reduce total chlorine and free chlorine contained in the pretreated water to zero whereby water to be treated was prepared. To this water

to be treated, combined chlorine agent obtained in Example 2 was added so that total chlorine concentration was 1.2 mg/L and free chlorine concentration 0.05 mg/L. The water to be treated was pressurized to 1.5 MPa by a pump and supplied to a concentrate room of a RO membrane treatment apparatus to carry out RO treatment. The RO membrane treatment apparatus was installed with one of 4 inch spiral type RO membrane element of aromatic polyamide ("ES 20 - D4" of Nitto Electric Industrial Co., Ltd) in a vessel.

[0036]

During 3 month continuous operation under the above condition, no deterioration of RO membrane, no increase of pressure drop and no slime trouble occurred. In the period, variations of permeate and pressure drop are shown in Fig. 2 and variation of salt rejection is shown in Fig. 3 wherein it is affirmed that there occurs no clogging by slime because there is no increase of pressure drop and no decrease of flux since the start of the operation. Further, it is also affirmed that there occurs no deterioration of water quality of produced water by adhesion of contaminant to RO membrane or deterioration of RO membrane because there occurs no decrease of salt rejection since the start of the operation.

[0037]

[Comparative Examples 9]:

Examples 4 was pursued except that pretreated water to be supplied to RO membrane was further added with a chlorine agent so that total chlorine concentration was 13 mg/L and free chlorine concentration 0.2 mg/L. In the period, variation of permeate and pressure drop is shown in Fig. 4 and variation of salt rejection is shown in Fig. 5 wherein it is recognized that there occurs

deterioration of RO membrane.

[0038]

[Comparative Examples 10]:

Examples 4 was pursued except that the water to be treated in the pretreatment was not added with a chlorine agent, and that pretreated water of free chlorine concentration of 0.0 mg/L was supplied to RO membrane. In the period, variations of permeate and pressure drop are shown in Fig. 6 and variation of salt rejection is shown in Fig. 7 wherein it is recognized that there occurs decrease of flux by slime formation.

Industrial Application of the Invention

[0039]

The present invention can be applied to a combined chlorine agent used for a slime control agent of reverse osmosis membrane and used for other chlorine treatment agents, method of production thereof and method of chlorine treatment as the use thereof, especially method of chlorine treatment for slime control of reverse osmosis membrane.

Claims

1. A combined chlorine agent comprising an aqueous agent which comprises alkali comprising alkali metal hydroxide, sulfamic acid or salt thereof, and oxidizing agent based on chlorine,

wherein the composition ratio of the oxidizing agent based on chlorine to the sulfamic acid or salt thereof is in the range from 0.45 to 0.6 by Cl / N (mole ratio),

the composition ratio of the oxidizing agent based on chlorine to alkali is in the range from 0.3 to 0.4 by Cl / alkali metal (mole ratio),

the composition ratio of sulfamic acid or salt thereof to alkali in the aqueous solution agent is in the range from 0.5 to 0.7 by N / alkali metal (mole ratio),

amount of alkali metal contained in salt of sulfamic acid is calculated as alkali,

pH of the aqueous agent is 13 or more, and

free chlorine concentration in the aqueous agent is 1000 mg/L or lower and 2 % by weight or lower of total chlorine concentration.

2. The combined chlorine agent as claimed in claim 1, wherein the combined chlorine agent is used for slime control agent of a reverse osmosis membrane.

3. A method of producing the combined chlorine agent as claimed in claim 1 or 2, comprising

adding sulfamic acid or salt thereof to an aqueous solution of alkali comprising alkali metal hydroxide to dissolve,

adding oxidizing agent based on chlorine to the obtained sulfamic acid - alkali aqueous mixture, and

mixing the finally obtained aqueous mixture to form an aqueous solution agent,

wherein the composition ratio of the oxidizing agent based on chlorine to the sulfamic acid or salt thereof is in the range from 0.45 to 0.6 by Cl / N (mole ratio),

the composition ratio of the oxidizing agent based on chlorine to alkali is in the range from 0.3 to 0.4 by Cl / alkali metal (mole ratio),

the composition ratio of sulfamic acid or salt thereof to alkali in the aqueous solution agent is in the range from 0.5 to 0.7 by N / alkali metal (mole ratio),

amount of alkali metal contained in salt of sulfamic acid is calculated as alkali,

pH of the aqueous agent is 13 or more, and

free chlorine concentration in the aqueous agent is 1000 mg/L or lower and 2 % by weight or lower of total chlorine concentration.

4. The method of producing the combined chlorine agent as claimed in claim 3, wherein the aqueous solution of alkali has a water content of 50 - 65 % by weight.

5. A method of chlorine treatment, comprising

adding the combined chlorine agent as claimed in claim 1 to a water system so that free chlorine concentration is 0.1 mg/L or lower and total chlorine concentration is 1 - 50 mg/L.

6. A method of chlorine treatment, comprising

adding the combined chlorine agent as claimed in claim 1 to a feed water system to a reverse osmosis membrane so that free chlorine concentration is 0.1 mg/L or lower and total chlorine concentration is 1 – 50 mg/L.