

SPECIFICATION

Title of Invention

Method of Membrane Separation

Technical Field

[0001]

The present invention relates to a method of membrane separation which is performed by supplying water to be treated to a membrane separation apparatus provided with a permeation membrane such as a reverse osmosis membrane (in the following sometimes called as "RO membrane"). More specifically, the present invention relates to a method of membrane separation wherein clogging of membrane by slime is efficiently prevented and stable treatment can be carried out for a long period of time by adding intermittently a combined chlorine agent comprising sulfamic compound to feed water supplied to a membrane separation apparatus.

Technical Background

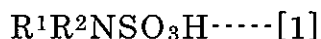
[0002]

When membrane separation by a permeation membrane such as a RO membrane is carried out for water to be treated containing suspended solid and organic matter together with contaminant substances such as microorganism, the permeation membrane is contaminated by these substances wherein clogging of membrane by slime adhesion occurs to decrease flux and separation rate. In

order to prevent the contamination of the membrane and to increase separation efficiency, there is adopted a slime adhesion prevention method wherein an oxidizing agent based on chlorine is added to feed water to be supplied to a membrane separation apparatus.

[0003]

Patent document 1 (JP2006-263510A) teaches slime prevention treatment without degradation of the membrane and without formation of trihalomethane wherein a stable combined chlorine agent comprising chlorosulfamate formed from an oxidizing agent based on chlorine and a sulfamic compound is added to feed water to be supplied to a membrane separation apparatus. The sulfamic compound is exemplified by sulfamic acid or salt thereof. The sulfamic acid is amidosulfuric acid represented by Formula [1] bellow wherein R^1 , R^2 denotes each H or hydrocarbon group having carbon number of 1-6 independently. The oxidizing agent based on chlorine is exemplified by chlorine gas, chlorine dioxide, hypochlorous acid and salt thereof.



[0004]

While patent document 1 suggests both continuous and intermittent additions of a sterilizing agent, continuous addition is adopted in Examples. Such continuous addition requires a large amount of chemicals causing high treatment costs. Further, even in case of continuous addition, low preventing effect of slime adhesion is obtained for the water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential.

[0005]

Patent document 2 (JP2010-201312A) teaches a method of

membrane separation by adding a combined chlorine agent comprising sulfamic compound to feed water supplied to a membrane separation apparatus wherein additive amount of the combined chlorine agent is periodically or irregularly increased to 2 - 10 times of ordinary amount for a period (T) and wherein Z value represented by the following Formula [2] is $1.0 < Z < 2.0$.

$$Z = (M_o \times T + M_x \times T_x) / (M_o \times T) \text{ ----- [2]}$$

(In Formula [2], M_o : Concentration of combined chlorine agent in feed water during ordinary concentration addition, T : Feeding period, M_x : Concentration of combined chlorine agent in feed water during 2 - 10 times concentration addition, T_x : Feeding period under concentration M_x .)

[0006]

Although, in Patent document 2, during continuous addition of a combined chlorine agent comprising sulfamic compound, high concentration addition is performed periodically or irregularly, low preventing effect of slime adhesion is obtained for the water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential. Considering the reason, if the proposed treatment is performed in the range of the increasing rate Z of $1.0 < Z < 2.0$, additive concentration during the high concentration addition period seems to be so important that the addition is carried out as high concentration as possible whereby the ordinary concentration addition period of low effect becomes longer causing increase of slime adhesion during the low effect period. On the contrary, if the low concentration period is set as short as possible, there comes out a problem that effect by addition at high concentration is almost lost because such concentration in the high concentration period cannot be heightened. In Patent document 2, since a

combined chlorine agent is added continuously, shock to microbes by intermittent changes in the concentration is small and exfoliating effect to already adhered slime is presumably small.

[0007]

Patent document 3 (JP2000-42544A) teaches a method of reverse osmosis membrane separation wherein a chlorine agent is added intermittently to the water to be treated under the condition that residual chlorine concentration at the moment of addition to the water to be treated is in the range of 0.2 - 10 mg/L as a concentration level not forming trihalomethane, that the adding rate I represented by the following Formula [3] is in the range of 0.01 - 0.95, and that residual chlorine concentration just before reverse osmosis membrane is in the range of 0.2 - 1 mg/L.

$$I = (T/1440) \times N \text{ ----- [3]}$$

(In Formula [3], T denotes adding period of chlorine agent (min), N is number of additions in 1 day.)

[0008]

In Patent document 3, since a chlorine agent is added intermittently at a low concentration level not forming trihalomethane, a low preventing effect of slime adhesion is obtained for the water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential. If a chlorine agent is added at high concentration in order to obtain effect, there comes out problems such as trihalomethane formation and deterioration of the membrane. Although, in Patent document 3, chlorine concentration varies by intermittent additions of sterilizer, shock to microbes by intermittent changes is small and exfoliating effect to already adhered slime is presumably small because a chlorine agent is added continuously to the water to be supplied to

membrane.

[0009]

Patent document 4 (JP2003-267811A) teaches a method of exfoliating slime wherein slime is exfoliated by adding to water system a slime exfoliating agent comprising an oxidizing agent based on chlorine and sulfamic acid and / or salt thereof. In Patent document 4, there are described that a slime control agent sterilizes or controls multiplication of microbe by denaturation of cell membrane, or by prohibition of enzyme reaction of bacteria, while a slime exfoliating agent disperses agglomerate of microbes to exfoliate slimes from adhered surfaces mainly by lowering adhesiveness of adhesive substances (usually polysaccharide) residing out side of microbe, and that the slime exfoliating agent of Patent document 4 has ability to lower adhesiveness of polysaccharide residing out side of microbe to reveal slime exfoliating effect.

[0010]

In Patent document 4, however, the method of exfoliating slime is applied only to the slime formed in ordinary water systems such as plant cooling water systems, paper - pulp water systems, waste treating water systems, iron - steel water systems, cutting oil water systems wherein there is no suggestion for application to slime exfoliation of permeation membrane such as RO membrane. Further, in Patent document 4, slime exfoliation is performed after slime adhesion has occurred. This means that the slime exfoliation is intended to be carried out in different process to prevention of slime adhesion. Since, in permeation by permeation membrane such as RO membrane, water as solvent permeates the membrane, microbe residing in the supplied water remains at the surfaces of the membrane to form biofilm. If the biofilm grows

into slime to adhere to the membrane surfaces, exfoliation of slime becomes to be difficult.

[0011]

In Non-patent document 1 (Microorganism Science 2), there is described that proliferation process of unicellular microorganism includes 1) Lag phase wherein cell count does not vary, 2) Acceleration phase wherein cell count increases gradually, 3) Logarithmic phase wherein cell count increases exponentially, 4) Retardation phase wherein specific proliferation rate lowers, 5) Stationary phase wherein increase and decrease of viable cell count come to a standstill, 6) Accelerating death phase wherein viable cell count begins to decrease then, and 7) Logarithmic death phase wherein viable cell count decreases exponentially. There is also described that, when chemical stress is given to microorganisms, action of the chemicals becomes stronger, as the concentration of the chemicals becomes higher, in such order as 1) No effect, 2) Acceleration of proliferation, 3) Inhibition of proliferation, 4) Sterilization. There are further described that proliferation rate decreases to zero at the inhibiting concentration for proliferation, and that increasing rate of cell number becomes minus at the sterilizing concentration whereby cell number decrease or becomes extinct. It is also described that, with regard to extinction, there is logarithm law of extinction wherein a linear relation is formed between duration and logarithm of viable cell count.

Prior Technical Document

[Patent Document]

[0012]

[Patent document 1] JP2006-263510A

[Patent document 2] JP2010-201312A

[Patent document 3] JP2000-42544A

[Patent document 4] JP2003-267811A

[Non-patent Document]

[0013]

[Non-patent document 1] Microorganism Science 2.,
Growth · Proliferation · Inhibition of Proliferation (Written by
Tomomichi YANAGIDA, Issued by Kabusikikaisha Gakkai Shuppan
Center on 20 March 1981)

Introduction of Invention

[Subject to be solved by Invention]

[0014]

An object of the present invention is to provide, in order to solve the above prior problem, a method of membrane separation wherein clogging of membrane by slime adhesion is efficiently prevented and stable treatment can be carried out for a long period of time at a low cost by a small amount of chemicals without stop of membrane separation for slime exfoliation and without the membrane deterioration and trihalomethane formation even if applied to the water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential.

[Means to solve Subject]

[0015]

The present invention includes the following methods of membrane separation:

- (1) A method of membrane separation, comprising
supplying water to be treated to a membrane separation

apparatus and

adding intermittently to the water to be treated a combined chlorine agent comprising sulfamic compound,

wherein viable cell count (log CFU/mL) of water to be treated is 3 or more,

the intermittent addition is performed by repeating a non-addition feeding period in which water to be treated is supplied without addition of combined chlorine agent, and an intermittent addition feeding period in which water to be treated is supplied under addition of a combined chlorine agent at biofilm exfoliating concentration in an early stage of biofilm formation during the non-addition feeding period,

the non-addition feeding period is for 6 - 120 hours,

the intermittent addition feeding period is for 0.5 - 40 hours,
and

the concentration of the combined chlorine agent in the water to be treated in the intermittent addition feeding period is 0.5 - 20 mg/L as total chlorine.

(2) The method of membrane separation according to the above (1), wherein additive amount of the combined chlorine agent added in the intermittent addition feeding period is the amount in which R represented by the following Formula [4] is 3 or more.

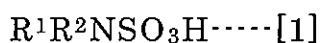
$$R = (\text{Intermittent addition feeding period (h)} \times [1000 \times \text{Intermittent addition concentration (mg-Cl/L)}]^{2.5} / (\text{Non-addition feeding period (h)}^{3.0} \times 10^{\log \text{CFU/mL}}) \quad [4]$$

(3) The method of membrane separation according to the above (1) or (2), wherein the early stage of biofilm formation to start the intermittent addition feeding is before logarithmic proliferation phase of microorganisms in the biofilm, and the biofilm exfoliating concentration is the concentration to inhibit

proliferation of microorganisms in the biofilm.

(4) The method of membrane separation according to any one of the above (1) to (3), wherein the membrane separation apparatus is provided with a reverse osmosis membrane.

(5) The method of membrane separation according to any one of the above (1) to (4), wherein sulfamic acid to form the sulfamic compound of the combined chlorine agent is amidosulfuric acid represented by the following Formula [1].



(In Formula [1], R^1, R^2 denote each H or hydrocarbon group having carbon number of 1-6 independently.)

(6) The method of membrane separation according to any one of the above (1) to (5), wherein the combined chlorine agent is an aqueous agent comprising alkali consisting of alkali metal hydroxide, sulfamic compound, and oxidizing agent based on chlorine,

wherein the composition ratio of the oxidizing agent based on chlorine to the sulfamic compound is in the range from 0.3 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 0.15 to 0.3 by Cl / alkali metal (mole ratio), and

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

[0016]

The membrane separation apparatus according to the present invention is provided with a permeation membrane wherein water to be treated is supplied to the permeation membrane to carry out membrane separation. As the permeation membrane, all membrane to be used for membrane separation, such

as RO membrane, UF membrane (ultrafiltration membrane), and MF membrane (microfiltration membrane), may be used, while a membrane separation apparatus provided with a RO membrane is preferable for the present invention. For the material of the permeation 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 permeation membrane may have a structure of module such as spiral type, hollow fiber type, tubular type, and flat membrane type.

[0017]

As to the water to be treated for membrane separation by supplying to the membrane separation apparatus, the present invention is applicable to all water possible to be separated by a permeation membrane, such as natural water, city water, industrial water, waste water, and treated water of waste water. The water to be treated may be water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential. The present invention is applied to water to be treated having viable cell count (log CFU/mL) of 3 or more and high slime adhesion potential whereby membrane separation can be performed under prevention of slime adhesion.

In the present invention, the viable cell count (log CFU/mL) of water to be treated is measured by sampling, in a sterilized bottle, a sample of water to be treated which is supplied to the membrane separation apparatus, leaving the sample as it is at 30 °C for 7 days, incubating the sample on an agar medium at 30 °C for 7 days, then counting the number of formed colonies on

the culture medium, and calculating log value of colony forming unit (CFU / mL). Here, "log" is used for common logarithm $\log_{10}$.
[0018]

According to the present invention, such water to be treated is supplied to a membrane separation apparatus and a combined chlorine agent comprising sulfamic compound is added intermittently to the water to be treated, whereby clogging of permeation membrane by growth of biofilm can be prevented efficiently and stable membrane separation can be carried out for a long period of time. Although intermittent addition of chlorine agent is known as shown in the Patent documents 1 and 3 and, similarly, combination of continuous and intermittent additions is also known, clogging of permeation membrane by adhesion of biofilm can not be prevented by simple application of intermittent additions as above. In membrane separation using a permeation membrane such as RO membrane, water as solvent permeates the membrane, while solute is concentrated at the surfaces of the membrane where remained microbe proliferates to form biofilm. If, by continuing the membrane separation in such condition, microbe further proliferates and biofilm grows into slime to adhere to the membrane surfaces, flux decreases by clogging of the membrane and exfoliation of slime becomes difficult.

[0019]

In an early stage of biofilm formation before logarithmic proliferation phase, especially in acceleration phase, adhesiveness of cells is so low that the biofilm can be exfoliated easily. On the contrary, in a latter stage of biofilm formation, especially after logarithmic proliferation phase, adhesiveness of cells is so high that slimes presumably adhere to the membrane to form clogging. According to the present invention, water to be treated is supplied

under intermittent addition of a combined chlorine agent at biofilm exfoliating concentration during a period when cell adhesiveness is low at an early stage of biofilm formation in the non-addition feeding period, namely before logarithmic proliferation phase, especially in acceleration phase, whereby biofilm can be exfoliated and clogging of membrane by growth of biofilm can be prevented. On the contrary, in the case that water to be treated is supplied under intermittent addition of a combined chlorine agent in a latter stage of biofilm formation, especially after logarithmic proliferation phase, it is difficult to exfoliate slimes having higher adhesiveness by growth of biofilm and clogging of membrane can not be prevented. Similar result is supposed applicable to the case wherein continuous addition and intermittent addition are combined.

[0020]

Non-patent document 1 reveals that proliferation rate can be forecasted computationally in logarithmic proliferation phase, namely logarithmic phase wherein cell count increases exponentially, that proliferation rate decreases at inhibiting concentration, and that increasing rate of cell count becomes 0 or minus at the sterilizing concentration whereby cell count decreases or becomes extinct. Accordingly, by stopping the non-addition feeding period at an early stage of biofilm formation during the non-addition feeding period, namely before logarithmic proliferation phase, especially in acceleration phase, and then by supplying water to be treated under addition of a combined chlorine agent at biofilm exfoliating concentration, biofilm can be exfoliated before the biofilm grows up to adhere to the membrane. Here, by calculating the amount of cells proliferated in biofilm until stopping of the non-addition feeding period and by supplying

water to be treated under addition of a combined chlorine agent at the amount to inhibit proliferation of cells in the biofilm, especially at the amount to decrease proliferation rate to 0 or minus, biofilm already proliferated can be exfoliated efficiently. By performing water supply under intermittent addition repeating non-addition feeding period and intermittent addition feeding period, biofilm can be exfoliated in a low adhesive condition of cells so that slime adhesion and clogging of membrane are prevented.

[0021]

In the present invention, a combined chlorine agent added to water to be treated is a combined chlorine agent comprising sulfamic compound. According to the present invention, free chlorine concentration, combined chlorine concentration, and total chlorine concentration are measured as Cl_2 concentration by DPD method using N,N-diethyle-1,4-phenylenediamine according to JIS K 0400-33-10:1999, which gives the following definitions. Namely, free chlorine is ruled as chlorine residing in forms of hypochlorous acid, hypochlorite ion or dissolved chlorine. Combined chlorine is also ruled as chlorine residing in forms of chloramine or organic chloramine which is included in total chlorine measured by the DPD method but not included in the free chlorine. Total chlorine is ruled as chlorine in forms of free chlorine and/or combined chlorine.

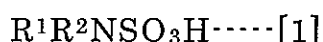
[0022]

A combined chlorine agent is an agent measured as the above combined chlorine which is preferably an aqueous agent comprising alkali consisting of alkali metal hydroxide, sulfamic compound, and oxidizing agent based on chlorine. A combined chlorine agent used in the present invention is exemplified in WO 2011/125762, a former application by the present applicant.

Especially, preferable agent is the one wherein the composition ratio of the oxidizing agent based on chlorine to the sulfamic compound is in the range from 0.3 to 0.6, preferably 0.4 - 0.5 by Cl / N (mole ratio), the composition ratio of the oxidizing agent based on chlorine to alkali is in the range from 0.15 to 0.3, preferably 0.2 - 0.25 by Cl / 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 compound to alkali in the aqueous solution agent is in the range from 0.4 to 0.6 by N / alkali metal (mole ratio). The above Cl / N (mole ratio) corresponds to the ratio of Cl₂ mole number of the oxidizing agent measured according to JIS K 0400-33-10:1999 to mole number of sulfamic compound composed of N. The above N / alkali metal (mole ratio) corresponds to the ratio of the above mole number of sulfamic compound to mole number of alkali metal formed by alkali metal hydroxide.

[0023]

Sulfamic acid to form the sulfamic compound of the combined chlorine agent is amidosulfuric acid represented by the following Formula [1].



(In Formula [1], R¹, R² denote each H or hydrocarbon group having carbon number of 1-6 independently.)

Preferable sulfamic acid is the one in narrow sense in which R¹, R² denote each H, while N-methyl sulfamic acid, N,N-dimethyl sulfamic acid, N-phenyl sulfamic acid, and so on may be used. Sulfamic compound may be sulfamic acid in powder of free acid or sulfamate such as alkali metal salt including sodium salt and potassium salt.

[0024]

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 an oxidizing agent based on chlorine becomes increased.

[0025]

The combined chlorine agent is produced by such a process wherein sulfamic compound is added to an aqueous solution of alkali consisting of alkali metal hydroxide to dissolve, and then an oxidizing agent based on chlorine is added to and mixed with the obtained aqueous mixture solution of sulfamic compound and alkali 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.

[0026]

Sulfamic compound may be added in the 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 compound is added in order that sulfamic compound concentration in the aqueous solution agent becomes to be the above concentration. Amount of sulfamic compound to be added is preferably the amount wherein composition ratio of sulfamic

compound to alkali is in the range from 0.4 to 0.6 by N / alkali metal (mole ratio). Sulfamic compound is 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 metal in Cl / alkali metal or N / alkali metal. In the case using an aqueous solution, amount of water contained in the aqueous solution is calculated as water in the aqueous solution of alkali.

[0027]

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 available chlorine (Cl_2) concentration in the aqueous solution agent becomes the above 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. In the case that the oxidizing agent based on chlorine is a salt of alkali metal, amount of the alkali metal is calculated as alkali metal in Cl / alkali metal or N / alkali metal.

[0028]

The above combined chlorine agent is used by adding to water to be treated 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 combined chlorine has higher permeability into biofilm than free chlorine, effects to lower stickiness of sticky substance from inside and to exfoliate biofilm can be obtained. In order to perform chlorine treatment, combined chlorine agent can be added, at a free chlorine concentration of 0.3 mg/L or lower, preferably 0.1 mg/L or lower, to water to be treated which is supplied to membrane separation apparatus. In this case, total chlorine concentration may be 0.5 - 20 mg/L.

[0029]

Even when the combined chlorine agent is added to water to be treated at a low free chlorine concentration as a slime control agent for permeation membrane such as RO membrane, combined chlorine concentration can be so high that available chlorine concentration becomes high and clogging of membrane by slime adhesion can be prevented, even in the case that the treatment applied to the water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential. In Patent document 3, since a chlorine agent is added intermittently at a low concentration level not forming trihalomethane, preventing effect of slime adhesion can not be obtained for the water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential. On the contrary, since the above combined chlorine agent can be added at a high combined chlorine concentration, slime adhesion can be prevented for the water to be treated having a large number of viable cell counts.

[0030]

Effect to prevent slime adhesion may be small when

combined chlorine agent is added continuously, as in Patent document 1, to water having a large number of viable cell counts and having water quality of harsh condition due to high slime adhesion potential, while biofilm can be exfoliated efficiently to obtain an effect of preventing slime adhesion by a small additive amount in the case that a combined chlorine agent is added intermittently according to the condition of the present invention. Since, in the case of continuous addition, treatment under similar conditions is carried out, already adhered slime grows without exfoliated. Since, however, in the case repeating non-addition feeding period and intermittent addition feeding period, microorganism in the already formed biofilm receives shocks, the biofilm is exfoliated whereby slime tends not to adhere as a whole. Although, in Patent document 2, slime receives shocks by heightening the concentration intermittently, slime layer becomes thick because a low concentration period continues a long period of time as 30 days whereby slime can not be exfoliated.

[0031]

In the present invention, biofilm can be exfoliated in a non-adhesive condition, by shortening the non-addition feeding period wherein no combined chlorine agent is added, and by intermittent addition feeding wherein a combined chlorine agent is added in a biofilm exfoliating concentration in which proliferation rate of microorganism is 0 or minus, at an early stage of biofilm formation, namely before logarithmic proliferation phase of microorganism in the biofilm, especially in acceleration phase. By this, slime adhesion can be prevented efficiently using small amount of chemicals for the water to be treated having a large number of viable cell counts. In order to carry out intermittent addition feeding at an early stage of biofilm formation according to

the present invention, non-addition feeding period adding no combined chlorine agent is performed for 6 - 120 hours, preferably 18 - 48 hours. Further, in order to control the combined chlorine concentration during the intermittent addition feeding period to an effective concentration wherein proliferation rate is 0 or minus, total chlorine concentration during the intermittent addition feeding period is controlled to 0.5 -20 mg/L, preferably 0.8 -16 mg/L, and duration of adding period to 0.5 -40 hours, preferably 1 -40 hours.

[0032]

According to the present invention, the additive amount of the combined chlorine agent to be added in the intermittent addition feeding period is the amount in which R represented by the following Formula [4] is 3 or more, preferably 5 or more, whereby biofilm formed in non-addition feeding period is exfoliated.

$$R = (\text{Intermittent addition feeding period (h)} \times [1000 \times \text{Intermittent addition concentration (mg-Cl/L)}]^{2.5} / (\text{Non-addition feeding period (h)}^{3.0} \times 10^{\log \text{CFU/mL}})) \quad [4]$$

(In Formula [4], Intermittent addition feeding period is indicated by hour (h), Intermittent addition concentration is indicated by total chlorine concentration (mg/L) when combined chlorine agent is added to water to be treated, Non-addition feeding period is indicated by hour (h), logCFU/mL is exponential number with viable cell count in the water to be treated.)

The above intermittent addition concentration is indicated by "mg-Cl/L". The exponential number with viable cell count indicated by "logCFU/mL" is given as a number corresponding "n" when viable cell count is shown as " $A \times 10^n/\text{mL}$ " wherein log is used for $\log_{10}$.

[0033]

The numerator of Formula [4] is the product of "Intermittent addition feeding period (h)" and "Intermittent addition concentration (mg-Cl/L)" which denotes additive amount of combined chlorine agent during the intermittent addition feeding period. The denominator of Formula [4] is the product of "Non-addition feeding period (h)" and "viable cell count indicated by (logCFU/mL)" which denotes proliferation amount of cells proliferated during the non-addition feeding period. Accordingly, R of Formula [4] is represented by (Additive amount of combined chlorine agent during the intermittent addition feeding period) / (proliferation amount during the non-addition feeding period), which denotes total amount of combined chlorine agent added during the intermittent addition feeding period to total amount of cells proliferated during the non-addition feeding period.

[0034]

Formula [4] has been developed from Non-patent document 1. Explaining proliferation during non-addition feeding period for denominator of R, the following Formula VI.5 is described, on page 243 of Non-patent document 1, relating to proliferation of unicellular microorganism in logarithmic phase.

$$\ln N = \ln N_0 + \mu t \text{ ----- (VI.5)}$$

(t: Time, N_0 : Cell number at $t=0$, N : Cell number at t , μ : Specific proliferation rate, $\ln$: natural logarithm $\log_e$.)

[0035]

Formula VI.5 is a formula relating to proliferation in logarithmic phase. In order to adapt to acceleration phase preceding logarithmic phase, the following Formula VI.5A has been developed by deciding exponential number of t as ($m=3$) according to Fig. VI.2 on page 242 of Non-patent document 1.

$$\ln N = \ln N_0 + \mu t^m \text{ -----}(m=3) \text{ -----(VI.5A)}$$

[0036]

Relating to specific proliferation rate μ , the following Formula VI.7 is described on page 244 of Non-patent document 1.

$$\mu_m \times S / (K_s + S) \text{ -----(VI.7)}$$

(μ_m : Maximum specific proliferation rate, S: Concentration of substrate, K_s : Specific proliferation rate at $(1/2) \mu_m$.)

[0037]

In Formula VI.7, "(Concentration of substrate S) = (Viable cell count)" is assumed because μ is proportional to Concentration of substrate S when Concentration of substrate S is small, and Concentration of substrate S is presumed to be high when viable cell count is large. For example, Concentration of substrate S is 10^4 when viable cell count ($\log CFU/mL$) = 4. In this manner, the formula of "proliferation amount of cells proliferated during the non-addition feeding period" in the denominator of Formula [4] is conducted from Formulas VI.5A and VI.7. This formula reveals proliferation amount of cells before logarithmic proliferation phase, especially in acceleration phase of proliferation of biofilm-forming microorganism during non-addition feeding period.

[0038]

Additive amount of combined chlorine agent during the intermittent addition feeding period represented by the numerator of Formula [4] is conducted as follows. Namely, the following Formula VII.5A is conducted by transforming Formula VII.5 bellow regarding reaction to chemical stress which is described on page 411 of Non-patent document 1.

$$(1/t) \times \ln (N_0/N) = K \times C^n \text{ -----(VII.5)}$$

$$\ln N = \ln N_0 - t \times K \times C^n \text{ -----(VII.5A)}$$

(K: Constant of proportion, C: Concentration of chemicals, n: Exponential number to sterilizing concentration.)

[0039]

Since Exponential number to sterilizing concentration varies with chemicals as about 1 for hypochlorous acid and 4 - 6 for phenol, the number in Formula VII.5 is set as $n = 2.5$ to meet Examples. By such manner, the formula of additive amount of combined chlorine agent during the intermittent addition feeding period represented by the numerator of Formula [4] has been conducted. While the formula reveals sterilizing concentration because "n" represents "Exponential number to sterilizing concentration", the formula can be recognized as concentration of chemicals to exercise chemical effect over viable cells because Formula VII.5 regards reaction to chemical stress. In the present invention, Formula VII.5A reveals exfoliation concentration of biofilm by permeation of chemicals because combined chlorine agent has high permeability.

[0040]

In the methods of membrane separation according to the present invention, membrane separation by supplying water to be treated to a membrane separation apparatus is performed, as explained before, by repeating a intermittent addition feeding period and a non-addition feeding period, wherein, in the intermittent addition feeding period, the water to be treated is supplied for 0.5 - 40 hours under addition of a combined chlorine agent comprising sulfamic compound at the total chlorine concentration of 0.5 - 20 mg/L, and, in the non-addition feeding period, the water to be treated is supplied for 6 - 120 hours under no addition of the combined chlorine agent. By adding the combined chlorine agent during the intermittent addition feeding

period at the amount in which R represented by the above Formula [4] is 3 or more, preferably 5 or more, low adhesive biofilm which has grown in the non-addition feeding period can be exfoliated efficiently by small amount of chemicals whereby slime trouble can be prevented.

[0041]

In the present invention, the non-addition feeding period adding no combined chlorine agent becomes short, by stopping the non-addition feeding period at an early stage of biofilm formation before logarithmic proliferation phase, especially in acceleration phase, and the intermittent addition feeding period reopens in a condition wherein adhesiveness of the proliferated cells is low and biofilm exfoliates easily. Further, by supplying to a permeation membrane in the intermittent addition feeding period, water to be treated having a combined chlorine concentration of a biofilm exfoliating concentration wherein proliferation rate is 0 or minus, biofilm can be exfoliated and growth of biofilm can be prevented whereby slime trouble can be prevented efficiently by small amount of chemicals even if applied to the water having a large number of viable cell counts.

[0042]

Since, in the present invention, by using the above combined chlorine agent, free chlorine concentration in water to be treated can be low even if combined chlorine concentration is heightened, slime adhesion is prevented and stable treatment of membrane separation can be continued without membrane deterioration and trihalomethane formation. Since combined chlorine agent is easily permeable to biofilm and exfoliative, biofilm exfoliation can be performed while continuing membrane separation in an early stage of biofilm formation. Accordingly, it is not necessary to stop

membrane separation for slime exfoliation.

[0043]

Although combined chlorine agent comprising sulfamic compound used in the present invention is exfoliative to slime, the exfoliative effect decreases remarkably when biofilm forming period of slime is long to form thick layers. Accordingly, it is important to set the concentration of the combined chlorine agent according to biofilm forming period (non-addition period) as above. Here, exfoliation of biofilm formed in one day is most efficient.

[Effect of Invention]

[0044]

According to the present invention, membrane separation is performed by supplying to membrane separation apparatus water to be treated having viable cell count (log CFU/mL) of 3 or more, and adding intermittently to the water to be treated a combined chlorine agent comprising sulfamic compound, wherein the intermittent additions of a combined chlorine agent to exfoliate biofilm are repeated at an early stage of biofilm formation in the non-addition feeding period, and wherein non-addition feeding period adding no combined chlorine agent is performed for 6 - 120 hours, the intermittent addition feeding period is performed for 0.5 - 40 hours, and concentration of combined chlorine agent during the intermittent addition feeding period is 0.5 - 20 mg/L as total chlorine concentration, whereby clogging of membrane by slime adhesion is efficiently prevented and stable treatment can be carried out for a long period of time at a low cost by a small amount of chemicals without stop of membrane separation for slime exfoliation and without the membrane deterioration and trihalomethane formation even if applied to the water having a large number of viable cell counts and having water quality of

harsh condition due to high slime adhesion potential.

Description of Drawings

[0045]

Fig. 1 is a flow diagram showing a method of membrane separation according to an embodiment of the present invention.

Means of putting the Invention into Practice

[Embodiment of Invention]

[0046]

Below, an embodiment of the present invention is explained by drawing. Fig. 1 is a flow diagram showing a method of membrane separation according to an embodiment of the present invention wherein numerous 1 denotes a filter, 2 an active carbon treatment apparatus, 3 a security filter, 4 a RO membrane separation apparatus, 5 a combined chlorine agent tank, 6 a reducing agent tank, 7 a control apparatus. Filter 1 is composed to filtrate through filter medium layer such as sand and anthracite to remove SS, colloid, and so on. Active carbon treatment apparatus 2 is composed to passage water through active carbon layer to remove organic matter, coloring substance, and so on. RO membrane separation apparatus 4 is composed to be divided to a concentrate chamber 4b and a permeate chamber 4c by a RO membrane module 4a to perform RO membrane separation. Control apparatus 7 is composed to repeat, by timing program, an intermittent addition feeding period wherein pump P1 is started, and a non-addition feeding period wherein pump P1 is stopped. Here, control apparatus 7 is composed to control additive amount

of combined chlorine agent by changing revolution rate of pump P1. Control apparatus 7 is also composed to control pump P2 by free chlorine detection signal of detector C.

[0047]

Membrane separation by the above apparatus is carried out as follows. During non-addition feeding period, pump P1 is stopped by a command from control apparatus 7. Water to be treated from raw water line L1 is supplied, without addition of combined chlorine agent from combined chlorine agent tank 5 via line L2, to filter 1 to filtrate, then to active carbon treatment apparatus 2 via line L3 to perform active carbon treatment, then to security filter 3 via line L4, and then to RO membrane separation apparatus 4 via line L5 to perform RO membrane separation.

[0048]

Intermittent addition feeding period starts at an early stage of biofilm formation in the non-addition feeding period, namely before logarithmic proliferation phase, wherein pump P1 is started by a command from control apparatus 7 to add a combined chlorine agent from combined chlorine agent tank 5 to the water to be supplied via line L2, and wherein revolution rate of pump P1 is controlled so that R represented by Formula [4] is at a designated value. By this, microorganisms in the water to be treated are sterilized. Then the water to be treated is subjected to filtration by filter 1, to active carbon treatment by active carbon treatment apparatus 2 via line L3, and, after passing security filter 3 via line L4, to RO membrane separation by RO membrane separation apparatus 4 via line L5, wherein microorganisms residing in and around the devices are also sterilized.

[0049]

During these processes, detector C installed in line L5

detects free chlorine concentration of the water to be treated at the exit of security filter 3. The detection signal is sent to control apparatus 7 which receives the free chlorine detection signal and controls pump P1 so that free chlorine concentration is 0.3 mg/L or lower. When the free chlorine concentration exceeds 0.3 mg/L even if additive amount of sulfamic compound is adjusted by controlling pump P1, control apparatus 7 controls pump P2, by the free chlorine detection signal of detector C, to add sodium bisulfite from reducing agent tank 6 via line L6. Active carbon treatment apparatus 2, reducing agent tank 6 and pump P2 may be omitted in some cases.

[0050]

After addition of combined chlorine agent has been continued for a designated period, pump P1 is stopped by a command from control apparatus 7 to repeat water supply of non-addition feeding period wherein RO membrane separation is carried out by continuing supply of water to be treated without addition of combined chlorine agent from combined chlorine agent tank 5. Since, by transferring to a new non-addition feeding period, microorganism proliferation reopens in a new environment, a new logarithmic proliferation phase of the microorganism restarts. Before the new logarithmic proliferation phase restarts, pump P1 is started by a command from control apparatus 7 to transfer to a new intermittent addition feeding period wherein biofilm formed during the preceding non-addition feeding period is exfoliated under low adhesive condition from the devices, especially RO membrane module 4a, whereby membrane clogging by biofilm growth can be prevented.

[Examples]

[0051]

Following is an explanation of Examples and Comparative Examples wherein % denotes "% by weight" unless specific indication is given. Viable cell count (log CFU / mL) was measured by the following method. Namely, 50 mL of the supplied water to RO membrane separation apparatus 4 was sampled in a 100 mL sterilized bottle from the exit of security filter 3 and left as it was at 30 °C for 7 days. Then 100 μ L of the sample was spread on an agar medium and incubated at 30 °C for 7 days. Then the number of formed colonies on the culture medium was counted to calculate viable cell count (log CFU / mL). The used agar medium was the most colony-forming culture medium selected from several different agar media.

[0052]

[Examples 1 - 13, Comparative Examples 1 - 3]:

Slime prevention treatment was carried out by supplying waste-treated water, as feed water, to RO membrane separation test apparatus for one month, and by adding, under the condition given in Table 1, intermittently to the feed water, combined chlorine agent comprising sulfamic compound which consists of an aqueous agent of pH 13 comprising 2 % (as available chlorine (Cl₂) concentration) of sodium hypochlorite, 8 % of sulfamic acid, and 1 % of sodium hydroxide. For the RO membrane, TW-30 [PA membrane], a product of The Dow Chemical Company was used. The experimental results obtained are given in Table 1.

[0053]

In Table 1, the effect of each Example was evaluated by flux maintaining rate for one month of water feeding, namely rate of the final flux to the first flux, wherein 95 - 100 % (final flux / first flux) was graded as ○, 90 - 94 % as △, and - 89 % as ×. "Viable cell count" in Table 1 denotes log value of viable cell count in 1 mL of

water to be treated (CFU / mL). "Concentration" denotes total chlorine concentration (mg·Cl/L) of water to be treated which is added by combined chlorine agent. "Adding rate I" is a number according to Formula [3] of Patent document 3 which was calculated for each Example. "Average concentration" is average concentration of oxidizing agent added in a unit period which is described as an index of treatment cost.

[0054]

[Table 1]

Table 1

	Viable cell count (log CFU/mL)	Non-addition feeding		Intermittent addition feeding		Increasing rate Z	Adding rate I	Average concentration (mg/L)	Effect	Additive amount of agent (numerator of R)	Proliferation amount of cell (denominator of R)	R
		Period (h)	Concentration (mg-Cl/L)	Period (h)	Concentration (mg-Cl/L)							
Comparative Example 1	3	21.0	0	3.0	0.4	-	0.13	0.0	×	8.7E+06	9.3E+06	1
Example 1	3	21.0	0	3.0	0.6	-	0.13	0.1	△	2.8E+07	9.3E+06	3
Example 2	3	21.0	0	3.0	0.8	-	0.13	0.1	○	4.9E+07	9.3E+06	5
Example 3	3	21.0	0	3.0	1.5	-	0.13	0.2	○	2.8E+08	9.3E+06	30
Example 4	3	23.0	0	1.0	1.5	-	0.04	0.1	○	9.3E+07	1.2E+07	8
Example 5	3	23.5	0	0.5	1.5	-	0.02	0.0	△	4.7E+07	1.3E+07	4
Comparative Example 2	3	23.9	0	0.1	1.5	-	0.00	0.0	×	9.3E+06	1.4E+07	1
Example 6	4	21.6	0	2.4	15.4	-	0.10	1.5	○	7.1E+10	1.0E+08	701
Example 7	4	19.2	0	4.8	7.7	-	0.20	1.5	○	2.5E+10	7.1E+07	353
Example 8	4	18.0	0	6.0	6.2	-	0.25	1.5	○	1.8E+10	5.8E+07	306
Example 9	4	22.5	0	1.5	3.1	-	0.06	0.2	○	7.9E+08	1.1E+08	7
Example 10	4	22.5	0	1.5	2.3	-	0.06	0.1	△	3.8E+08	1.1E+08	3
Example 11	4	6.0	0	6.0	6.2	-	0.25	3.1	○	1.8E+10	2.2E+06	8273
Example 12	4	48.0	0	16.0	6.2	-	-	1.5	○	4.8E+10	1.1E+09	43
Example 13	4	120.0	0	40.0	6.2	-	-	1.5	○	1.2E+11	1.7E+10	7
Comparative Example 3	4	240.0	0	80.0	6.2	-	-	1.5	×	2.4E+11	1.4E+11	2

[0055]

In Table 1, inferior results were obtained for examples beyond the present invention such as Comparative Example 1 wherein additive concentration during the intermittent addition feeding period was low and R is 1, Comparative Example 2 wherein the intermittent addition feeding period was short and R was 1, and Comparative Example 3 wherein the intermittent addition feeding period was long and R was 2. Although Comparative Example 1 adopts adding rate I of 0.01 - 0.95 which was rated as a suitable rate according to Patent document 3, no effect was obtained in the case that viable cell count (logCFU/mL) was 3 or more.

[0056]

On the contrary, Example 1 - 3 showed that good effect of treatment was obtained at low cost (low average concentration) in the case of intermittent additive concentration at 0.6 mg - Cl / L or higher. Example 4 - 5 showed that duration of intermittent addition feeding period was suitable to be 0.5 h or more. Example 6 - 10 showed that additive concentration over 10 mg - Cl / L was disadvantageous in cost, despite that there was no upper limit of additive concentration for prevention effect. From Example 11 - 13, duration of non-addition feeding period was favorable to be 6 h - 120 h, because in the case that non-addition feeding period was short, average concentration became higher causing disadvantage in cost, and in the case that non-addition feeding period exceeds 120 h, no effect was obtained which required high concentration addition causing deterioration of permeate and increase in salt concentration with added chemicals.

[0057]

[Comparative Examples 4 - 14]:

The procedures as in Examples 1 - 11 and Comparative

Examples 1 - 3 were pursued except that combined chlorine agent was added as Example 1 of Patent document 2 wherein ordinary addition for 29 days and high concentration addition for one day were performed by varying additive concentration. The experimental results were shown in Table 2 wherein "Increasing rate Z " denotes value calculated according to Formula [2] of Patent document 2. Other items in Table 2 were the same as Table 1.

[0058]

[Table 2]

Table 2

	Viable cell count (logCFU/mL)	Ordinary concentration addition		High concentration addition		Increasing rate Z	Adding rate I	Average concentration (mg/L)	Effect	R
		Period (d)	Concentration (mg-Cl/L)	Period (d)	Concentration (mg-Cl/L)					
Comparative Example 4	2	29	3.9	1	15	1.13	-	4.2	○	-
Comparative Example 5	2	29	1.5	1	15	1.33	-	2.0	○	-
Comparative Example 6	2	29	0.8	1	15	1.67	-	1.3	○	-
Comparative Example 7	2	29	0.4	1	12	2.00	-	0.8	○	-
Comparative Example 8	3	29	3.9	1	15	1.13	-	4.2	○	-
Comparative Example 9	3	29	1.5	1	15	1.33	-	2.0	○	-
Comparative Example 10	3	29	0.8	1	15	1.67	-	1.3	○	-
Comparative Example 11	3	29	0.4	1	12	2.00	-	0.8	×	-
Comparative Example 12	4	29	3.9	1	15	1.13	-	4.2	○	-
Comparative Example 13	4	29	1.5	1	15	1.33	-	2.0	×	-
Comparative Example 14	4	29	0.8	1	15	1.67	-	1.3	×	-

[0059]

In Table 2, it is understood that the additive manner of Patent document 2 is effective in the case that water to be treated has low (=2) viable cell count (logCFU/mL) corresponding to slime adhesion potential as shown in Comparative Examples 4 - 7, but ineffective in the case that water to be treated has high viable cell count (logCFU/mL) as shown in Comparative Examples 8 - 14.

Method of Industrial Application of the Invention

[0060]

The present invention can be applied to a method of membrane separation which is performed by supplying water to be treated to a membrane separation apparatus provided with a permeation membrane such as a reverse osmosis membrane, especially, to a method of membrane separation wherein clogging of membrane by slime is efficiently prevented and stable treatment can be carried out for a long period of time by adding intermittently an oxidizing agent based on combined chlorine comprising sulfamic compound to feed water supplied to a membrane separation apparatus.

[Explanation of Numeral]

[0061]

1: Filter, 2: Active carbon treatment apparatus, 3: Security filter, 4: RO membrane separation apparatus, 4a: RO membrane module, 4b: Concentrate chamber, 4c: Permeate chamber, 5: Combined chlorine agent tank, 6: Reducing agent tank, 7: Control apparatus, C: Detector, L1: Raw water line, L2 - L8: Line, P1 - P2: Pump.

CLAIMS

1. A method of membrane separation, comprising
supplying water to be treated to a membrane separation
apparatus and

adding intermittently to the water to be treated a combined
chlorine agent comprising sulfamic compound,

wherein viable cell count (log CFU/mL) of water to be
treated is 3 or more,

the intermittent addition is performed by repeating a
non-addition feeding period in which water to be treated is
supplied without addition of combined chlorine agent, and an
intermittent addition feeding period in which water to be treated is
supplied under addition of a combined chlorine agent at biofilm
exfoliating concentration in an early stage of biofilm formation
during the non-addition feeding period,

the non-addition feeding period is for 6 - 120 hours,

the intermittent addition feeding period is for 0.5 - 40 hours,
and

the concentration of the combined chlorine agent in the
water to be treated in the intermittent addition feeding period is
0.5 - 20 mg/L as total chlorine.

2. The method of membrane separation as claimed in claim 1,
wherein additive amount of the combined chlorine agent added in
the intermittent addition feeding period is the amount in which R
represented by the following Formula [4] is 3 or more.

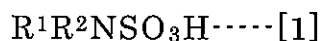
$$R = (\text{Intermittent addition feeding period (h)} \times [1000 \times \text{Intermittent addition concentration (mg-Cl/L)}]^{2.5} / (\text{Non-addition feeding period (h)}^{3.0} \times 10^{\log \text{CFU/mL}})) \quad [4]$$

3. The method of membrane separation as claimed in claim 1 or

2, wherein the early stage of biofilm formation to start the intermittent addition feeding is before logarithmic proliferation phase of microorganisms in the biofilm, and the biofilm exfoliating concentration is the concentration to inhibit proliferation of microorganisms in the biofilm.

4. The method of membrane separation as claimed in any one of the claims 1 to 3, wherein the membrane separation apparatus is provided with a reverse osmosis membrane.

5 The method of membrane separation as claimed in any one of claims 1 to 4, wherein sulfamic acid to form the sulfamic compound of the combined chlorine agent is amidosulfuric acid represented by the following Formula [1].



(In Formula [1], R^1, R^2 denote each H or hydrocarbon group having carbon number of 1-6 independently.)

6. The method of membrane separation as claimed in any one of claims 1 to 5, wherein the combined chlorine agent is an aqueous agent comprising alkali consisting of alkali metal hydroxide, sulfamic compound, and oxidizing agent based on chlorine,

wherein the composition ratio of the oxidizing agent based on chlorine to the sulfamic compound is in the range from 0.3 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 0.15 to 0.3 by Cl / alkali metal (mole ratio), and

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