

DESCRIPTION

MEMBRANE FILTRATION METHOD AND MEMBRANE FILTRATION SYSTEM

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TECHNICAL FIELD

[0001]

The present invention relates to a membrane filtration method and a membrane filtration system.

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BACKGROUND

[0002]

Conventionally, wastewater treatments in which a flocculant is added to a water to be treated to perform a flocculation and settling treatment or a dissolved air flotation treatment are already known (for example, see Patent Document 1).

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CITATION LIST

PATENT LITERATURE

[0003]

Patent Document 1: JP H11-57313 A

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SUMMARY

TECHNICAL PROBLEM

[0004]

However, if an ultrafiltration membrane or microfiltration membrane is used on a treated water that has been prepared by performing a flocculation and settling treatment or dissolved air flotation treatment using a flocculant, then a phenomenon (fouling) sometimes occurs in which the surface of the membrane becomes contaminated and the membrane pores become blocked. Accordingly, an object of the present invention is to

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provide a membrane filtration method and a membrane filtration system which can suppress fouling of an ultrafiltration membrane or microfiltration membrane and enable stable operation when used with a treated water that has been prepared by performing a flocculation and settling treatment or dissolved air flotation treatment using a flocculant.

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SOLUTION TO PROBLEM

[0005]

(1) One aspect of an embodiment of the present invention is a membrane filtration method that includes adding a coagulant to a treated water, said treated water having been prepared by adding a flocculant to a water to be treated and performing a flocculation and settling treatment or a flocculation and dissolved air flotation treatment, and performing at least one membrane filtration treatment among an ultrafiltration membrane treatment and a microfiltration membrane treatment.

[0006]

(2) In the membrane filtration method described above in (1), at the time of the membrane filtration treatment, it is preferable that at least one of application of a shearing force to the treated water and addition of an oxidant to the treated water is performed, so that the average molecular weight of the flocculant in the treated water is not more than the molecular weight cutoff of the membrane used in the membrane filtration treatment.

20 [0007]

(3) In the membrane filtration method described above in (1) or (2), the amount added of the coagulant is preferably within a range from 0.5 times to 75 times the concentration (mg/L) of the flocculant in the water to be treated.

[0008]

(4) In the membrane filtration method described above in any one of (1) to (3), the amount added of the coagulant is preferably controlled in accordance with the concentration of polymeric organic matter detected by LC-OCD in the treated water that

has undergone the flocculation and settling treatment or the flocculation and dissolved air flotation treatment.

[0009]

5 (5) In the membrane filtration method described above in any one of (1) to (4), at least one post-treatment among an activated carbon treatment and a reverse osmosis membrane treatment is preferably performed on the treated water that has undergone the membrane filtration treatment.

[0010]

10 (6) In the membrane filtration method described above in any one of (1) to (5), at the time of the membrane filtration treatment, the pH of the treated water is preferably controlled so that the Langelier saturation index (LSI) of the treated water is less than 0.

[0011]

15 (7) One aspect of an embodiment of the present invention is a membrane filtration system that includes a coagulant addition unit for adding a coagulant to a treated water, said treated water having been prepared by adding a flocculant to a water to be treated and performing a flocculation and settling treatment or a flocculation and dissolved air flotation treatment, and a membrane filtration treatment unit which has at least one of an ultrafiltration membrane and a microfiltration membrane, and performs a membrane filtration treatment of the treated water to which the coagulant has been added.

20 [0012]

(8) The membrane filtration system described above in (7) preferably includes at least one of a shearing force application unit for applying a shearing force to the treated water and an oxidant addition unit for adding an oxidant to the treated water at the time of the membrane filtration treatment, wherein at least one of application of the shearing force and addition of the oxidant ensures that the average molecular weight of the flocculant in
25 the treated water is not more than the molecular weight cutoff of the membrane used in the membrane filtration treatment.

[0013]

(9) In the membrane filtration system described above in (7) or (8), the amount added of the coagulant is preferably within a range from 0.5 times to 75 times the concentration (mg/L) of the flocculant in the water to be treated.

[0014]

5 (10) The membrane filtration system described above in any one of (7) to (9) preferably has a post-treatment unit for performing a post-treatment on the treated water that has undergone the membrane filtration treatment, wherein the post-treatment unit is preferably at least one of an activated carbon treatment unit and a reverse osmosis membrane treatment unit.

10 [0015]

(11) The membrane filtration system described above in any one of (7) to (10) preferably includes a pH control unit for controlling the pH of the treated water so that, at the time of the membrane filtration treatment, the Langelier saturation index (LSI) of the treated water is less than 0.

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ADVANTAGEOUS EFFECTS OF INVENTION

[0016]

The membrane filtration method and membrane filtration system according to embodiments of the present invention can suppress fouling and enable stable operation of an ultrafiltration membrane or microfiltration membrane when used with a treated water that has been prepared by performing a flocculation and settling treatment or a dissolved air flotation treatment using a flocculant.

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BRIEF DESCRIPTION OF DRAWINGS

25 [0017]

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

FIG. 2 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment of the present invention.

FIG. 3 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment of the present invention.

5 FIG. 4 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment of the present invention.

FIG. 5 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment of the present invention.

10 FIG. 6 is a schematic diagram illustrating the structure of a treatment system in a reference example.

FIG. 7 is a diagram illustrating the results for the filtration resistance ($1/m$) relative to the filtration volume (m^3/m^2) for the membrane filtration device in Examples 1 and 2, and Comparative Examples 1 and 2.

15 FIG. 8 is a diagram illustrating the results for the filtration resistance ($1/m$) relative to the filtration volume (m^3/m^2) for the membrane filtration device in Example 3 and Comparative Example 3.

FIG. 9 is a diagram illustrating the results for the filtration resistance ($1/m$) relative to the filtration volume (m^3/m^2) for the membrane filtration device in Example 4 and Comparative Example 4.

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DESCRIPTION OF EMBODIMENTS

[0018]

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

[0019]

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

illustrated in FIG. 1 includes a flocculation and settling system and a membrane filtration system. The flocculation and settling system contains a first flocculation reaction tank 10, a flocculant addition line 12, and a floc settling tank 14. The membrane filtration system contains a coagulant addition device 15 and a coagulant addition line 16 as one example of a coagulant addition unit, a second flocculation reaction tank 18, and a membrane filtration device 20 as one example of a membrane filtration treatment unit.

[0020]

A water to be treated line 22 is connected to an inlet of the first flocculation reaction tank 10. Further, one end of a connection line 24a is connected to an outlet of the first flocculation reaction tank 10, with the other end being connected to an inlet of the floc settling tank 14, one end of a connection line 24b is connected to an outlet of the floc settling tank 14, with the other end being connected to an inlet of the second flocculation reaction tank 18, and one end of a connection line 24c is connected to an outlet of the second flocculation reaction tank 18, with the other end being connected to an inlet of the membrane filtration device 20. Furthermore, an outlet of the membrane filtration device 20 is connected to a treated water line 26. The flocculant addition line 12 is connected to the first flocculation reaction tank 10. Further, one end of the coagulant addition line 16 is connected to the coagulant addition device 15, with the other end being connected to the second flocculation reaction tank 18.

[0021]

The coagulant addition device 15 is composed of a tank that houses the coagulant, a pump that discharges the coagulant, and a valve or the like. The coagulant supplied from the coagulant addition device 15 passes through the coagulant addition line 16 and is supplied to the second flocculation reaction tank 18. Examples of the coagulant used in the present embodiment include polyaluminum chloride (PACL), aluminum sulfate, ferric chloride, ferric sulfate, and aluminum chloride.

[0022]

Examples of the flocculant used in the present embodiment include polymeric flocculants such as polyacrylamide-based flocculants, polysulfonic acid-based flocculants, polyacrylic acid-based flocculants, polyacrylate ester-based flocculants, polyamine-based flocculants and polymethacrylic acid-based flocculants, and low-molecular weight flocculants (coagulants) such as surfactants. The flocculant is, for example, supplied from a flocculant addition device not shown in the figure, passes through the flocculant addition line 12, and is supplied to the first flocculation reaction tank 10.

[0023]

The membrane filtration device 20 contains at least one of a UF membrane device provided with an ultrafiltration membrane, and an MF membrane device provided with a microfiltration membrane. The UF membrane device or MF membrane device is, for example, composed of at least one module having the ultrafiltration membrane or microfiltration membrane housed inside a sealable container. There are no particular limitations on the shape of the ultrafiltration membrane or microfiltration membrane, and possible shapes include hollow fiber membranes, tubular membranes, flat membranes, and spiral membranes. The method used for passing water through the membrane filtration device 20 may employ any water supply method, including internal pressure-type methods and external pressure-type methods, and any filtration method may be applied, including cross-flow filtration and dead-end filtration.

[0024]

Examples of the material of the ultrafiltration membrane or microfiltration membrane include organic membranes such as polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyethersulfone (PES) and cellulose acetate (CA), and inorganic membranes such as ceramics.

[0025]

The molecular weight cutoff of the ultrafiltration membrane is, for example, typically within a range from 5,000 to 360,000, and is preferably within a range from 10,000 to 360,000. The pore size of the ultrafiltration membrane is, for example, within a

range from 0.01 μm to 0.1 μm , and is preferably within a range from 0.01 μm to 0.03 μm . The pore size of the microfiltration membrane is, for example, within a range from 0.1 μm to 0.5 μm , and is preferably within a range from 0.1 μm to 0.2 μm .

[0026]

5 There are no particular limitations on the water to be treated that is treated by the treatment system 1, and examples include raw water containing impurities such as suspended solids and scale components such as calcium, and specific examples of the water to be treated include industrial wastewater (for example, wastewater from plating systems or the like), tap water, ground water (for example, well water, spring water and
10 subsoil water), and surface water (for example, river water and lake water).

[0027]

One example of the operation of the treatment system 1 of the present embodiment is described below.

[0028]

15 The water to be treated passes through the water to be treated line 22 and is supplied to the first flocculation reaction tank 10, while the flocculant is supplied from the flocculant addition line 12 to the first flocculation reaction tank 10. Inside the first flocculation reaction tank 10, the water to be treated and the flocculant are stirred with a stirrer 28a, and the impurities such as suspended solids within the water to be treated
20 undergo flocculation. Subsequently, the water to be treated containing the flocculant passes through the connection line 24a and is supplied to the floc settling tank 14, and the flocculated impurities such as suspended solids are allowed to settle as a sludge.

[0029]

The supernatant passes through the connection line 24b and is supplied to the second
25 flocculation reaction tank 18 as a treated water that has undergone the flocculation and settlement treatment. Further, the coagulant is supplied from the coagulant addition device 15, through the coagulant addition line 16, to the second flocculation reaction tank 18. Inside the second flocculation reaction tank 18, the treated water and the coagulant

are stirred with a stirrer 28b, bringing any residual flocculant within the treated water into contact with the coagulant. The treated water containing the added coagulant passes through the connection line 24c and is introduced into the membrane filtration device 20. Impurities within the treated water are trapped by the filtration membrane such as the ultrafiltration membrane or microfiltration membrane inside the membrane filtration device 20, and the treated water from which the impurities have been removed is discharged from the treated water line 26. The thus obtained treated water may be used, for example, as wash water or the like in food processing plants, chemical plants, semiconductor plants, and machinery plants and the like.

10 [0030]

The membrane filtration device 20 is backwashed periodically using the treated water obtained from the membrane filtration treatment or the like, and the impurities that have accumulated on the membrane surface are either discharged from the system together with the backwash wastewater, or are fed into the floc settling tank 14. In terms of enabling settling and separation of the suspended solids in the backwash wastewater, and in terms of improving the water recovery ratio (the ratio of treated water volume/supplied water volume, with this water recovery ratio decreasing if the wastewater is discharged from the system), the backwash wastewater is preferably fed into the floc settling tank 14.

15 [0031]

20 Usually, if treated water containing a flocculant is subjected to a membrane filtration treatment with an ultrafiltration membrane or a microfiltration membrane or the like, then the flocculant accumulates on the membrane surface, and fouling of the membrane tends to occur easily. However, in the present embodiment, it is thought that by bringing the coagulant into contact with the flocculant, the coagulant adheres to the flocculant,

25 converting the flocculant to a form that is less likely to adhere to the membrane surface, or a form that can be easily detached from the membrane surface by backwashing or the like. Accordingly, by adding the coagulant and then performing the membrane filtration treatment, fouling of the membrane can be suppressed, and more stable operation can be

achieved, compared with the case where the membrane filtration treatment is performed without adding the coagulant. However, although a system could be considered in which, during the flocculation and settling treatment using a flocculant, a coagulant is added together with the flocculant, even in this type of system, a certain amount of the flocculant (for example, flocculant to which the coagulant has not adhered) remains in the treated water obtained from the flocculation and settling treatment, and therefore achieving satisfactory suppression of membrane fouling is more difficult, and achieving a stable treatment is more difficult, compared with the method of the present embodiment in which the coagulant is added to the treated water that has undergone the flocculation and settling treatment, and the membrane filtration treatment is then performed.

[0032]

There are no particular limitations on the amount added of the coagulant, provided it is an amount that can suppress membrane fouling, but for example, an amount of the coagulant that is within a range from 0.5 times to 75 times the concentration (mg/L) of the flocculant in the water to be treated is preferable, and from the viewpoint of economic viability, an amount within a range from 0.5 times to 2.5 times is more preferable. If the amount added of the coagulant is less than 0.5 times, then it is thought that membrane fouling may not be satisfactorily suppressed, whereas if the amount exceeds 75 times, then it is thought that filtration resistance caused by floc derived from the coagulant may increase. Accordingly, ensuring that the amount satisfies the above range enables membrane fouling to be more effectively suppressed, compared with the case where the amount does not satisfy the above range.

[0033]

In the present embodiment, a treated water obtained from a flocculation and settling treatment using a flocculant was described, but similar effects can be obtained for a treated water obtained from a flocculation and dissolved air flotation treatment using a flocculant. The flocculation and dissolved air flotation treatment may, for example, be a

conventionally known dissolved air flotation treatment or the like (for example, see JP 5239653 B).

[0034]

In terms of improving the contact rate between the flocculant and the coagulant, a flocculation reaction tank (the second flocculation reaction tank 18 illustrated in FIG.1) is preferably provided, but in terms of reducing installation space and the like, a treatment system such as that illustrated in FIG. 2, in which a flocculation reaction tank is not provided, and the coagulant addition line 16 is installed on the connection line 24b, with the coagulant undergoing line injection, may also be used.

[0035]

FIG. 3 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment. In the treatment system 3 illustrated in FIG. 3, those structures that are the same as those of the treatment system 1 illustrated in FIG. 1 are labeled with the same reference signs, and description of those structures is omitted.

The treatment system 3 illustrated in FIG. 3 is configured so that, at the time of the membrane filtration treatment, an oxidant is added to the treated water that has undergone the flocculation and settling treatment (or flocculation and dissolved air flotation treatment). Specifically, the treatment system 3 illustrated in FIG. 3 includes an oxidant addition device 29 and an oxidant addition line 30 as an oxidant addition unit, and the oxidant passes through the oxidant addition line 30 from the oxidant addition device 29, and is added to the second flocculation reaction tank 18. Addition of the oxidant may also be performed by the type of line injection illustrated in FIG. 2.

[0036]

In those cases where a polymeric flocculant such as a polyacrylamide-based flocculant is used as the flocculant, the average molecular weight (the weight average molecular weight or the number average molecular weight) of the flocculant is typically larger than the molecular weight cutoff of the ultrafiltration membrane or microfiltration membrane used in the subsequent stage. If a flocculant having a molecular weight that

exceeds the molecular weight cutoff of the membrane remains in the treated water, then the flocculant has an effect on membrane fouling. The molecular weight cutoff is determined as the molecular weight corresponding with a rejection rate of 90% when a standard substance having a known molecular weight is supplied to the membrane, and for example
5 if a treated water containing a polymeric flocculant having a molecular weight exceeding 5,000 is supplied to an ultrafiltration membrane or microfiltration membrane having a molecular weight cutoff of 5,000, then at least 90% of the polymeric flocculant will be trapped by the membrane.

[0037]

10 Accordingly, in the treatment system 3 illustrated in FIG. 3, by adding the oxidant to the treated water at the time of the membrane filtration treatment, the molecular chains of the flocculant are cleaved, and the molecular weight of the flocculant is reduced to a value no higher than the molecular weight cutoff of the ultrafiltration membrane or microfiltration membrane, and preferably a value smaller than the molecular weight cutoff.
15 As a result, a portion of the flocculant is not trapped by the membrane, and the flocculant passes through the membrane together with the treated water, and therefore compared with the case in which only a coagulant is added, membrane fouling can be better suppressed.

[0038]

Examples of the oxidant include alkali metal salts of hypochlorous acid such as
20 sodium hypochlorite and potassium hypochlorite, alkaline earth metal salts of hypochlorous acid such as calcium hypochlorite and barium hypochlorite, alkali metal salts of chlorous acid such as lithium chlorite, sodium chlorite and potassium chlorite, alkaline earth metal salts of chlorous acid such as calcium chlorite and barium chlorite, other metal salts of chlorous acid such as nickel chlorite, alkali metal salts of chloric acid such as
25 ammonium chlorate and sodium chlorate, and alkaline earth metal salts of chloric acid such as calcium chlorate.

[0039]

There are no particular limitations on the amount added of the oxidant, provided it is an amount that can reduce the molecular weight of the flocculant to a value no higher than the molecular weight cutoff of the membrane, but for example, an amount of the oxidant that is within a range from 0.5 times to 75 times the concentration (mg/L) of the flocculant in the water to be treated prior to flocculation and settling is preferable, and an amount from 0.5 times to 2.5 times is more preferable.

[0040]

Further, the amount added of the coagulant is preferably controlled in accordance with the concentration of polymeric organic matter detected by LC-OCD in the treated water that has undergone the flocculation and settling treatment or flocculation and dissolved air flotation treatment. LC-OCD is a technique that fractionates organic matter by molecular weight, displaying peaks for polymeric organic matter, humic substances, humic degradation products, low-molecular weight organic acids, and low-molecular weight organic matter and the like in terms of retention time, with the concentration corresponding with each peak able to be quantified.

[0041]

It is thought that polymeric organic matter contributes to membrane blockages, and therefore by ascertaining in detail the concentration of polymeric organic matter within the organic matter in the treated water that has undergone the flocculation and settling treatment or flocculation and dissolved air flotation treatment, the amount added of the coagulant can be set to a more appropriate amount. By increasing or decreasing the amount added of the coagulant in accordance with the size of the peak for polymeric organic matter detected by LC-OCD, running costs can be reduced.

[0042]

Other methods for reducing the molecular weight of the flocculant, besides adding an oxidant, include a method in which shearing force is applied to the treated water. The stirrer 28b provided in the second flocculation reaction tank 18 is an example of a shearing force application unit, and by stirring the treated water and imparting a shearing force, the

molecular chains of the flocculant can be cleaved, reducing the molecular weight of the flocculant to a value no higher than the molecular weight cutoff of the ultrafiltration membrane or microfiltration membrane. For example, by adjusting the stirring speed and the stirring time and the like, the molecular weight of the flocculant can be reduced to a value no higher than the molecular weight cutoff of the ultrafiltration membrane or microfiltration membrane. The stirring speed setting used for reducing the molecular weight of the flocculant is, for example, typically within a range from 200 rpm to 1,000 rpm, and is preferably within a range from 700 rpm to 1,000 rpm. Further, the stirring time used for reducing the molecular weight of the flocculant is, for example, typically within a range from 5 minutes to 1 hour, and is preferably within a range from 30 minutes to 1 hour.

[0043]

FIG. 4 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment. In the treatment system 4 illustrated in FIG. 4, those structures that are the same as those of the treatment system 1 illustrated in FIG. 1 are labeled with the same reference signs, and description of those structures is omitted. The treatment system 4 illustrated in FIG. 4 includes an activated carbon device 32 filled with activated carbon and a reverse osmosis membrane device 34 provided with a reverse osmosis membrane at a subsequent stage to the membrane filtration device 20. One end of a treated water line 26a is connected to an outlet of the membrane filtration device 20, and the other end is connected to an inlet of the activated carbon device 32. Further, one end of a treated water line 26b is connected to an outlet of the activated carbon device 32, and the other end is connected to an inlet of the reverse osmosis membrane device 34. A permeate line 36 is connected to the permeate outlet of the reverse osmosis membrane device 34, and a concentrate line 38 is connected to the concentrate outlet.

[0044]

The reverse osmosis membrane used in the present embodiment is a membrane that can remove ion components in the treated water, and also includes nanofiltration

membranes (NF). There are no particular limitations on the shape of the reverse osmosis membrane, and possible shapes include hollow fiber membranes, tubular membranes, flat membranes, and spiral membranes. Examples of the material of the reverse osmosis membrane include polyamide-based materials, piperazine amide-based materials, and
5 cellulose acetate-based materials.

[0045]

In the treatment system illustrated in FIG. 4, the treated water discharged from the membrane filtration device 20 passes through the treated water line 26a, and is supplied to the activated carbon device 32. Following the removal of impurities in the treated water
10 by the activated carbon device 32, the treated water is supplied from the treated water line 26b to the reverse osmosis membrane device 34, and is separated into a permeate and a concentrate. The permeate (treated water) obtained from the reverse osmosis membrane device 34 is discharged from the permeate line 36. The thus obtained permeate may be
15 used, for example, not only as wash water or the like in food processing plants, chemical plants, semiconductor plants, and machinery plants and the like, but also as dilution water, drinking water, recycled water, air conditioning water, raw water for pure water production, rinsing raw water, and water for steam production and the like. The concentrate obtained
from the reverse osmosis membrane device 34 is discharged from the concentrate line 38, and may, for example, be stored in a storage tank not shown in the figure.

20 [0046]

The treatment system illustrated in FIG. 4 is provided with both the activated carbon device 32 and the reverse osmosis membrane device 34, but depending on the targeted water quality and the like for the final treated water, a selection may be made as to whether only the activated carbon device 32 is installed, only the reverse osmosis membrane device
25 34 is installed, or both the activated carbon device 32 and the reverse osmosis membrane device 34 are installed. Although omitted from the description relating to the figures, the activated carbon device 32 and/or the reverse osmosis membrane device 34 may also be installed in the treatment systems illustrated in FIG. 2 and FIG. 3.

[0047]

FIG. 5 is a schematic diagram illustrating one example of the structure of a treatment system according to another embodiment of the present invention. In the treatment system 5 illustrated in FIG. 5, those structures that are the same as those of the treatment system 1 illustrated in FIG. 1 are labeled with the same reference signs, and description of those structures is omitted. The treatment system 5 illustrated in FIG. 5 includes a pH control system as one example of a pH control unit. The pH control system is provided with a pH regulator addition device 40, a pH regulator addition line 42, a water quality detection device 44, and a control unit 46.

10 [0048]

The pH regulator addition device 40 is, for example, composed of a tank for storing the pH regulator, a pump for discharging the pH regulator, and a valve or the like. One end of the pH regulator addition line 42 is connected to the pH regulator addition device 40, and the other end is connected to the second flocculation reaction tank 18.

15 [0049]

The water quality detection device 44 has a pH sensor, a temperature sensor, an electrical conductivity sensor, a calcium hardness sensor and a total alkalinity sensor, and detects the pH value, the water temperature, the electrical conductivity, the calcium hardness and the total alkalinity of the treated water in the second flocculation reaction tank 18.

[0050]

The control unit 46 contains a processor and memory, and has a Langelier saturation index calculation section 48 and a pH regulator amount control section 50 as functional blocks. The various detection values detected by the water quality detection device 44 are input into the Langelier saturation index calculation section 48. Based on the Langelier saturation index calculated by the Langelier saturation index calculation section 48, the pH regulator amount control section 50 calculates the amount of the pH regulator to

be added, and controls the amount of the pH regulator added by the pH regulator addition device 40.

[0051]

The processor of the control unit 46 executes various processes, such as a process for calculating the Langelier saturation index and a process for controlling the amount added of the pH regulator, in accordance with process programs stored in the memory. One example of the operation of the control unit 46 is described below.

[0052]

The Langelier saturation index calculation section 48 calculates the Langelier saturation index of the treated water based on the detected value detected by the water quality detection device 44. The Langelier saturation index (LSI) is typically calculated from the following formula (1).

$$\text{LSI} = \text{pH} - \text{pHs} \quad (1)$$

[0053]

In formula (1), pH represents the pH value of the treated water. Further, pHs represents the theoretical pH value when calcium carbonate in the treated water is in an equilibrium state, undergoing neither dissolution nor precipitation, and is calculated from the following formula (2).

$$\text{pHs} = 9.3 + \text{A value} + \text{B value} - \text{C value} - \text{D value} \quad (2)$$

[0054]

In formula (2), the A value is a correction value determined by the evaporation residue concentration. The evaporation residue concentration correlates with the electrical conductivity, and therefore the evaporation residue concentration can be calculated from the electrical conductivity using a prescribed conversion formula. The B value is a correction value determined by the water temperature. The C value is a correction value determined by the calcium hardness. The D value is a correction value determined by the total alkalinity. The A to D values can be determined from the detected

values from the water quality detection device 44, either using either relational formulas or with reference to numerical tables.

[0055]

The Langelier saturation index is a general index used for evaluating the tendency for scale formation in a water system, and for positive values, a larger absolute value indicates a tendency for calcium carbonate to precipitate more easily, whereas for negative values, a larger absolute value indicates that calcium carbonate is less likely to precipitate. Further, when the Langelier saturation index is 0, an equilibrium state is achieved in which neither precipitation nor dissolution of calcium carbonate occurs. Based on these definitions, when the Langelier saturation index of the treated water is less than 0, scale caused by calcium carbonate is unlikely to form on the membrane surface of the ultrafiltration membrane or the microfiltration membrane, whereas in contrast, when the Langelier saturation index exceeds 0, scale caused by calcium carbonate is likely to form on the membrane surface.

[0056]

Accordingly, when the calculated Langelier saturation index of the treated water is 0 or greater, the pH regulator amount control section 50 sets the amount of pH regulator to be added so as to alter the Langelier saturation index of the treated water to a value less than 0. The pH regulator addition device 40 then adds the pH regulator to the treated water based on this set amount of pH regulator to be added, thereby altering the Langelier saturation index of the treated water to a value less than 0. As is clear from formula (1), the Langelier saturation index of the treated water decreases as the pH of the treated water falls, and increases as the pH rises. Accordingly, the Langelier saturation index of the treated water can be controlled by adjusting the pH of the treated water.

[0057]

The treatment system 5 of the present embodiment is, for example, effective as a system for treating wastewater that contains fluorine. In a flocculation and settling treatment or a dissolved air flotation treatment of a wastewater containing fluorine (the

water to be treated), in order to recover the fluorine, a calcium agent is sometimes added together with flocculant to the water to be treated. Accordingly, the treated water obtained from this type of settling treatment or dissolved air flotation treatment may sometimes contain calcium, and the Langelier saturation index of the treated water is likely to be 0 or greater. As a result, scale can sometimes form on the ultrafiltration membrane or the microfiltration membrane. However, in the present embodiment, as described above, by controlling the pH of the treated water so that the Langelier saturation index of the treated water is less than 0 (and becomes a negative value), scale production is suppressed. Accordingly, membrane fouling can be better suppressed, and more stable operation can be achieved. Although omitted from the description relating to the figures, a pH control system may also be installed in the treatment systems illustrated in FIG. 2 to FIG. 4.

[0058]

(Reference Example)

FIG. 6 is a schematic diagram illustrating the structure of a treatment system in a reference example. In the treatment system 6 illustrated in FIG. 6, those structures that are the same as those of the treatment system 1 illustrated in FIG. 1 are labeled with the same reference signs, and description of those structures is omitted. The treatment system 6 illustrated in FIG. 6 is configured so that when the membrane filtration treatment is performed, a coagulant is not added to the treated water that has undergone the flocculation and settling treatment (or flocculation and dissolved air flotation treatment), but rather an oxidant is added from the oxidant addition device 29, through the oxidant addition line 30, and into the second flocculation reaction tank 18. The addition of the oxidant may also be performed via the type of line injection illustrated in FIG. 2.

[0059]

In the treatment system illustrated in FIG. 6, by adding the oxidant to the treated water at the time of the membrane filtration treatment, the molecular chains of the flocculant are cleaved, and the molecular weight of the flocculant is reduced to a value no

higher than the molecular weight cutoff of the ultrafiltration membrane or microfiltration membrane, and preferably a value smaller than the molecular weight cutoff. As a result, a portion of the flocculant is not trapped by the membrane, and the flocculant passes through the membrane together with the treated water, and therefore compared with the case in which only a coagulant is added, membrane fouling can be better suppressed.

[0060]

There are no particular limitations on the amount added of the oxidant, provided it is an amount that can reduce the molecular weight of the flocculant to a value no higher than the molecular weight cutoff of the membrane, but for example, an amount of the oxidant that is within a range from 2.5 times to 100 times the concentration (mg/L) of the flocculant in the water to be treated is preferable, and an amount from 20 times to 50 times is more preferable.

[0061]

Other methods for reducing the molecular weight of the flocculant, besides adding an oxidant, include a method in which shearing force is applied to the treated water. The stirrer 28b provided in the second flocculation reaction tank 18 is an example of a shearing force application unit, and by stirring the treated water and imparting a shearing force, the molecular chains of the flocculant can be cleaved, reducing the molecular weight of the flocculant to a value no higher than the molecular weight cutoff of the ultrafiltration membrane or microfiltration membrane. The stirring speed setting used for reducing the molecular weight of the flocculant is, for example, typically within a range from 200 rpm to 1,000 rpm, and is preferably within a range from 700 rpm to 1,000 rpm. Further, the stirring time used for reducing the molecular weight of the flocculant is, for example, typically within a range from 5 minutes to 1 hour, and is preferably within a range from 30 minutes to 1 hour. Although omitted from the description relating to the figures, the treatment system illustrated in FIG. 6 may also be applied to the treatment systems illustrated in FIGS. 2 to 5.

EXAMPLES

[0062]

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

[0063]

(Example 1)

Using the treatment system illustrated in FIG. 1, a plating system wastewater having the water quality shown in Table 1 was treated.

10 [0064]

[Table 1]

Plating system wastewater	
pH	9.5
TOC (mg/L)	0.97
Fe (mg/L)	204

[0065]

A UF membrane device was used as the membrane filtration device of Example 1.

15 Details of the UF membrane device were as follows.

Dimensions: outer diameter: 230 mm × height: 2,400 mm

Filtration surface area (membrane surface area): 77 m²

Ultrafiltration membrane: hollow fiber membrane made from PVDF, nominal pore size: 0.01 μm (nominal molecular weight cutoff: 360,000 Da)

20 Filtration method: external pressure dead-end filtration

Treatment flow rate: 9.6 m³/h

[0066]

To the plating system wastewater having the water quality shown in Table 1 was added 1.0 ppm of a polyacrylamide-based polymer as a flocculant, and after performing a

flocculation and settling treatment, the supernatant was supplied to the second flocculation reaction tank. Following the addition of 75 ppm of ferric chloride as a coagulant to the second flocculation reaction tank, the water was supplied to the membrane filtration device (UF membrane device), and a membrane filtration treatment was performed.

5 [0067]

(Example 2)

With the exception of altering the amount of the coagulant (ferric chloride) from 75 ppm to 10 ppm, the same treatments as Example 1 were performed.

[0068]

10 (Comparative Example 1)

With the exception of not adding the coagulant (ferric chloride), the same treatments as Example 1 were performed.

[0069]

(Comparative Example 2)

15 With the exceptions of altering the amount of the flocculant (polyacrylamide-based polymer) from 1.0 ppm to 0.5 ppm, and not adding the coagulant (ferric chloride), the same treatments as Example 1 were performed.

[0070]

20 The water quality results for the treated waters obtained following the membrane filtration treatment in Examples 1 and 2, and Comparative Examples 1 and 2 are shown in Table 2. Further, FIG. 7 illustrates the results for the filtration resistance (1/m) relative to the filtration volume (m^3/m^2) for the membrane filtration device in Examples 1 and 2, and Comparative Examples 1 and 2.

[0071]

25 [Table 2]

	Example 1	Example 2	Comparative Example 1	Comparative Example 2
pH	5.9	5.9	9.3	9.4

TOC (mg/L)	0.71	0.75	0.98	0.93
Fe (mg/L)	< 0.05	< 0.05	< 0.05	< 0.05

[0072]

As illustrated in FIG. 7, compared with Comparative Examples 1 and 2 in which the membrane filtration treatment was performed without adding the coagulant to the treated water, Examples 1 and 2 in which a coagulant was added, before the membrane filtration treatment was performed, to the treated water obtained from the flocculation and settling treatment using the flocculant, any increase in the filtration resistance was suppressed even when the filtration volume was increased. The rate of increase in the filtration resistance relative to the increase in the filtration volume indicates the deterioration in filtration performance as a result of membrane fouling. Accordingly, the treatment methods of Examples 1 and 2 were able to suppress membrane fouling and enable stable operation. Considering the fact that Comparative Example 1, in which the amount added of the flocculant was greater than the amount in Comparative Example 2, exhibited a higher rate of increase in the filtration resistance than Comparative Example 2, it can be stated that the residual flocculant in the treated water is contributing to membrane fouling. On the other hand, in Examples 1 and 2, although the same amount of the flocculant as Comparative Example 1 was added, almost no increase in the filtration resistance occurred even when the filtration volume was increased, indicating that membrane fouling was being suppressed. It is thought that this is because adding the coagulant converted the flocculant in the treated water to a form that was less likely to adhere to the membrane surface.

[0073]

Further, as shown in Table 2, in Examples 1 and 2, the TOC values for the treated water were reduced, confirming that the residual flocculant had been treated.

[0074]

(Example 3)

With the exceptions of altering the amount of the flocculant (polyacrylamide-based polymer) from 1.0 ppm to 5.0 ppm, and altering the amount of the coagulant (ferric chloride) from 75 ppm to 2.5 ppm, the same treatments as Example 1 were performed.

[0075]

5 (Comparative Example 3)

One ppm of ferric chloride as a coagulant was added together with 5.0 ppm of the polyacrylamide-based polymer as a flocculant to the plating system wastewater having the water quality shown in Table 1, and following a flocculation and settling treatment, the supernatant was passed directly into the membrane filtration device (the UF membrane
10 device described above), and a membrane filtration treatment was performed.

[0076]

The water quality results for the treated waters obtained following the membrane filtration treatment in Example 3 and Comparative Example 3 are shown in Table 3.

[0077]

15

[Table 3]

	Example 3	Comparative Example 3
pH	5.9	5.9
TOC (mg/L)	0.81	0.84
Fe (mg/L)	< 0.05	< 0.05

[0078]

FIG. 8 illustrates the results for the filtration resistance (1/m) relative to the filtration
5 volume (m^3/m^2) for the membrane filtration device in Example 3 and Comparative
Example 3. The rate of increase in the filtration resistance in Example 3 was similar to
that observed in Example 1 and Example 2. In contrast, the rate of increase in the
filtration resistance in Comparative Example 3 was higher than that observed in Example 3
in which the amount added of the coagulant was the same, but was lower than that
10 observed in Comparative Examples 1 and 2 in which the coagulant was not added. Based
on these results, it can be stated that in order to better suppress membrane fouling, it is
necessary to add the coagulant to the treated water that has been prepared by performing a
flocculation and settling treatment using the flocculant.

[0079]

15 (Example 4)

With the exceptions of changing the coagulant from ferric chloride to polyaluminum
chloride (PACL), and altering the amount added from 75 ppm to 50 ppm, the same
treatments as Example 1 were performed.

[0080]

20 (Comparative Example 4)

With the exception of altering the time of sampling of the raw water, the same
treatments as Comparative Example 1 were performed.

[0081]

FIG. 9 illustrates the results for the filtration resistance ($1/m$) relative to the filtration volume (m^3/m^2) for the membrane filtration device in Example 4 and Comparative Example 4. In Example 4, in which PACL was used as the coagulant, in a similar manner to Examples 1 to 3, there was almost no increase in the filtration resistance even when the filtration volume was increased, and membrane fouling was suppressed. In contrast, in Comparative Example 4, in which no coagulant was added, the filtration resistance increased as the filtration volume increased.

[0082]

(Examples 5 to 10)

Using the treatment system illustrated in FIG.1, a simulated wastewater was treated. The simulated wastewater contained 10 mg/L of bentonite dispersed in tap water. The membrane filtration device was the same UF membrane device as that used in Example 1.

[0083]

In Example 5, 1.0 ppm of a polyacrylic acid-based polymer (OX-304 (a cationic polymer), manufactured by Organo Corporation) was added as a flocculant to the above simulated wastewater, a flocculation and settling treatment was performed, and the supernatant was then supplied to the second flocculation reaction tank. Following the addition of 10 ppm of PACL as a coagulant to the second flocculation reaction tank, the water was supplied to the membrane filtration device (UF membrane device), and a membrane filtration treatment was performed.

[0084]

In Example 6, with the exception of changing the flocculant from the polyacrylic acid-based polymer (OX-304 (a cationic polymer), manufactured by Organo Corporation) to an acrylamide-based polymer (AP-1 (an anionic polymer), manufactured by Organo Corporation), a membrane filtration treatment was performed in the same manner as Example 5.

[0085]

In Example 7, with the exception of changing the flocculant from the polyacrylic acid-based polymer (OX-304 (a cationic polymer), manufactured by Organo Corporation) to a polyacrylamide-based polymer (ON-1H (a nonionic polymer), manufactured by Organo Corporation), a membrane filtration treatment was performed in the same manner as Example 5.

[0086]

In Example 8, with the exception of changing the coagulant from PACL to ferric chloride (FeCl_3), a membrane filtration treatment was performed in the same manner as Example 5.

[0087]

In Example 9, with the exception of changing the coagulant from PACL to ferric chloride (FeCl_3), a membrane filtration treatment was performed in the same manner as Example 6.

[0088]

In Example 10, with the exception of changing the coagulant from PACL to ferric chloride (FeCl_3), a membrane filtration treatment was performed in the same manner as Example 7.

[0089]

(Comparative Examples 5 to 7)

In Comparative Example 5, with the exception of not adding the coagulant, a membrane filtration treatment was performed in the same manner as Example 5.

[0090]

In Comparative Example 6, with the exception of not adding the coagulant, a membrane filtration treatment was performed in the same manner as Example 6.

[0091]

In Comparative Example 7, with the exception of not adding the coagulant, a membrane filtration treatment was performed in the same manner as Example 7.

[0092]

In Examples 5 to 10 and Comparative Examples 5 to 7, the time (filtration time) taken from the start of water supply to the membrane filtration device until 200 ml of filtrate was obtained was measured. The results are shown in Table 4. A longer filtration time means a faster increase in the filtration resistance.

5 [0093]

[Table 4]

	Organic flocculant	Coagulant	Filtration time (seconds)
Example 5	Polyacrylic acid-based	PACL	183
Example 6	Acrylamide-based	PACL	174
Example 7	Polyacrylamide-based	PACL	178
Example 8	Polyacrylic acid-based	FeCl ₃	178
Example 9	Acrylamide-based	FeCl ₃	185
Example 10	Polyacrylamide-based	FeCl ₃	178
Comparative Example 5	Polyacrylic acid-based	-	225
Comparative Example 6	Acrylamide-based	-	384
Comparative Example 7	Polyacrylamide-based	-	465

[0094]

10 Examples 5 to 10 in which a flocculant and a coagulant were added each exhibited a shorter filtration time compared with Comparative Examples 5 to 7 in which only a flocculant was added. In other words, it can be stated that in Examples 5 to 10, any increase in filtration resistance was better suppressed than in Comparative Examples 5 to 7.

REFERENCE SIGNS LIST

15 [0095]

1 to 6: Treatment system

10: First flocculation reaction tank

- 12: Flocculant addition line
- 14: Floc settling tank
- 15: Coagulant addition device
- 16: Coagulant addition line
- 5 18: Second flocculation reaction tank
- 20: Membrane filtration device
- 22: Water to be treated line
- 24a to 24c: Connection line
- 26, 26a, 26b: Treated water line
- 10 28a, 28b: Stirrer
- 29: Oxidant addition device
- 30: Oxidant addition line
- 32: Activated carbon device
- 34: Reverse osmosis membrane device
- 15 36: Permeate line
- 38: Concentrate line
- 40: pH regulator addition device
- 42: pH regulator addition line
- 44: Water quality detection device
- 20 46: Control unit
- 48: Langelier saturation index calculation section
- 50: pH regulator amount control section

CLAIMS

1. A membrane filtration method comprising: adding a coagulant to a treated water, said treated water having been prepared by adding a flocculant to a water to be treated and performing a flocculation and settling treatment or a flocculation and dissolved air flotation treatment; and performing at least one membrane filtration treatment among an ultrafiltration membrane treatment and a microfiltration membrane treatment,

wherein the flocculant comprises at least one of polyacrylamide-based flocculants, polysulfonic acid-based flocculants, polyacrylic acid-based flocculants, polyacrylate ester-based flocculants, polyamine-based flocculants and polymethacrylic acid-based flocculants, and

wherein at a time of the membrane filtration treatment, at least one of application of a shearing force to the treated water by stirring the treated water with a stirrer within a range from 200 rpm to 1,000 rpm and addition of an oxidant to the treated water is performed, so that an average molecular weight of the flocculant in the treated water is not more than a molecular weight cutoff of a membrane used in the membrane filtration treatment.

2. The membrane filtration method according to Claim 1, wherein an amount added of the coagulant is within a range from 0.5 times to 75 times a concentration (mg/L) of the flocculant in the water to be treated.

3. The membrane filtration method according to any one of Claims 1 to 2, wherein an amount added of the coagulant is controlled in accordance with a concentration of polymeric organic matter detected by LC-OCD in the treated water that has undergone the flocculation and settling treatment or flocculation and dissolved air flotation treatment.

4. The membrane filtration method according to any one of Claims 1 to 3, wherein at least one post-treatment among an activated carbon treatment and a reverse osmosis membrane treatment is performed on a treated water that has undergone the membrane filtration treatment.

5. The membrane filtration method according to any one of Claims 1 to 4, wherein at a time of the membrane filtration treatment, a pH of the treated water is controlled so that a Langelier saturation index (LSI) of the treated water is less than 0.

5 6. A membrane filtration system comprising:

a coagulant addition unit for adding a coagulant to a treated water, said treated water having been prepared by adding a flocculant to a water to be treated and performing a flocculation and settling treatment or a flocculation and dissolved air flotation treatment, and

a membrane filtration treatment unit which has at least one of an ultrafiltration
10 membrane and a microfiltration membrane, and performs a membrane filtration treatment of the treated water to which the coagulant has been added, and

at least one of a shearing force application unit for applying a shearing force to the treated water by stirring the treated water within a range from 200 rpm to 1,000 rpm and an oxidant addition unit for adding an oxidant to the treated water at a time of the membrane
15 filtration treatment,

wherein the flocculant comprises at least one of polyacrylamide-based flocculants, polysulfonic acid-based flocculants, polyacrylic acid-based flocculants, polyacrylate ester-based flocculants, polyamine-based flocculants and polymethacrylic acid-based flocculants, and

20 wherein at least one of application of the shearing force and addition of the oxidant ensures that an average molecular weight of the flocculant in the treated water is not more than a molecular weight cutoff of a membrane used in the membrane filtration treatment.

25 7. The membrane filtration system according to Claim 6, wherein an amount added of the coagulant is within a range from 0.5 times to 75 times a concentration (mg/L) of the flocculant in the water to be treated.

8. The membrane filtration system according to any one of Claims 6 and 7,

30 having a post-treatment unit for performing a post-treatment on a treated water that has undergone the membrane filtration treatment, wherein

the post-treatment unit is at least one of an activated carbon treatment unit and a reverse osmosis membrane treatment unit.

9. The membrane filtration system according to any one of Claims 6 to 8, further
5 comprising a pH control unit for controlling a pH of the treated water so that, at a time of the membrane filtration treatment, a Langelier saturation index (LSI) of the treated water is less than 0.