

DESCRIPTION

METHOD FOR TREATING AMMONIACAL NITROGEN-CONTAINING WASTEWATER AND AMMONIACAL NITROGEN DECOMPOSER

5

TECHNICAL FIELD

[0001]

The present invention relates to a method for treating ammoniacal
nitrogen-containing wastewater that is used for treating wastewater such as sewage that
10 contains ammoniacal nitrogen, and also relates to an ammoniacal nitrogen decomposer.

BACKGROUND

[0002]

When workplace wastewater including industrial wastewater or treated water from
15 sewage or the like is discharged into public water systems, the discharged water is required
to conform with the wastewater standards prescribed in the Water Pollution Control Law.
Further, in the case of the three ocean areas composed of Tokyo Bay, Ise Bay and the
Inland Sea of Japan, the discharged water must also satisfy total pollutant restrictions for
COD, nitrogen and phosphorus.

20 [0003]

Among the various types of wastewater, sewage and wastewater from fish
processing plants and the like must be disinfected prior to discharge to reduce the coliform
bacteria count to not more than 3,000 /ml, so as to conform with wastewater standards and
total pollutant restrictions, and the amounts of those components such as ammoniacal
25 nitrogen that are subjected to wastewater restrictions are preferably reduced as far as
possible.

[0004]

Examples of disinfectants that are typically used for sewage and the like include chlorine-based oxidizing agents such as hypochlorite salts, but if the water to be treated contains ammoniacal nitrogen, then these chlorine-based oxidizing agents tend to react with the ammoniacal nitrogen to produce chloramine, meaning the disinfectant effect may be insufficient. Accordingly, bromine-based oxidizing agents have recently been proposed for use as disinfectant components. If a component capable of decomposing ammoniacal nitrogen contained in the wastewater is used as a disinfectant component, then this can lead to a reduced load on subsequent biological treatments such as nitrification-denitrification processes, enabling a more advantageous wastewater treatment.

[0005]

Patent Document 1 discloses a disinfectant containing hypobromous acid or a salt thereof as a disinfectant for wastewater such as sewage. Further, Patent Document 2 discloses a method for disinfecting discharged sewage containing ammonia or ammonium ions that uses a solid disinfectant formed from 1-bromo-3-chloro-5,5-dimethylhydantoin, and this method can also be applied to the treatment of sewage-containing rainwater.

[0006]

However, the method disclosed in Patent Document 1 requires storage facilities for the two chemical reagents, namely the bromide salt and the hypochlorite salt used to obtain the hypobromous acid or salt thereof, as well as a reaction device in which to react the two reagents, meaning the equipment is very large. In the method disclosed in Patent Document 2, because the disinfectant is a solid, a dissolution device is required, which results in a similar increase in the size of the equipment. Further, in the methods disclosed in Patent Documents 1 and 2, absolutely no mention is made regarding the reduction effect on ammoniacal nitrogen contained in the wastewater or sewage or the like.

CITATION LIST

PATENT LITERATURE

[0007]

Patent Document 1: JP 2003-012425 A

Patent Document 2: JP 4628132 B

SUMMARY

5 TECHNICAL PROBLEM

[0008]

An object of the present invention is to provide a method for treating ammoniacal nitrogen-containing wastewater and an ammoniacal nitrogen decomposer that are capable of treating ammoniacal nitrogen-containing wastewater using a simple method.

10

SOLUTION TO PROBLEM

[0009]

The present invention provides a method for treating an ammoniacal nitrogen-containing wastewater, the method including incorporating a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based

15 oxidizing agent (reaction components composed of a bromine compound and a chlorine-based oxidizing agent), and a sulfamic acid compound, in an ammoniacal nitrogen-containing wastewater containing ammoniacal nitrogen.

[0010]

20

The present invention also provides a method for treating an ammoniacal nitrogen-containing wastewater, the method including incorporating a mixture or a reaction product of a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound, in an ammoniacal nitrogen-containing wastewater containing ammoniacal nitrogen.

25

[0011]

The present invention also provides a method for treating an ammoniacal nitrogen-containing wastewater, the method including incorporating a mixture of bromine and a sulfamic acid compound, or incorporating a reaction product of bromine and a

sulfamic acid compound, in an ammoniacal nitrogen-containing wastewater containing ammoniacal nitrogen.

[0012]

5 In the method for treating an ammoniacal nitrogen-containing wastewater described above, after incorporating the bromine-based oxidizing agent, or the reaction product of a bromine compound and a chlorine-based oxidizing agent, and the sulfamic acid compound, in the ammoniacal nitrogen-containing wastewater, the treated water containing a reduced amount of ammoniacal nitrogen is preferably further treated with a reverse osmosis membrane.

10 [0013]

In the method for treating an ammoniacal nitrogen-containing wastewater described above, after incorporating the mixture or the reaction product of the bromine-based oxidizing agent, or the reaction product of a bromine compound and a chlorine-based oxidizing agent, and the sulfamic acid compound, in the ammoniacal nitrogen-containing wastewater, the treated water containing a reduced amount of ammoniacal nitrogen is preferably further treated with a reverse osmosis membrane.

[0014]

20 In the method for treating an ammoniacal nitrogen-containing wastewater described above, after incorporating the mixture of bromine and the sulfamic acid compound, or after incorporating the reaction product of bromine and the sulfamic acid compound, in the ammoniacal nitrogen-containing wastewater, the treated water containing a reduced amount of ammoniacal nitrogen is preferably further treated with a reverse osmosis membrane.

[0015]

25 In the methods for treating an ammoniacal nitrogen-containing wastewater described above, the ratio of the equivalent weight of the sulfamic acid compound relative to the equivalent weight of bromine is preferably within a range from 0.5 to 1.5.

[0016]

In the methods for treating an ammoniacal nitrogen-containing wastewater described above, the ratio of the molar concentration of effective halogen, calculated as an effective chlorine concentration, relative to the molar concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater, is preferably 1.6 or greater.

5 [0017]

In the methods for treating an ammoniacal nitrogen-containing wastewater described above, the concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater is preferably 5 mg/L or greater.

[0018]

10 The present invention also provides an ammoniacal nitrogen decomposer for decomposing ammoniacal nitrogen in an ammoniacal nitrogen-containing wastewater, wherein the ammoniacal nitrogen decomposer contains a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound.

15 [0019]

The present invention also provides an ammoniacal nitrogen decomposer for decomposing ammoniacal nitrogen in an ammoniacal nitrogen-containing wastewater, wherein the ammoniacal nitrogen decomposer contains a mixture or a reaction product of a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound.

[0020]

The present invention also provides an ammoniacal nitrogen decomposer for decomposing ammoniacal nitrogen in an ammoniacal nitrogen-containing wastewater, wherein the ammoniacal nitrogen decomposer contains a mixture of bromine and a sulfamic acid compound, or a reaction product of bromine and a sulfamic acid compound.

25 [0021]

In the ammoniacal nitrogen decomposers described above, the ratio of the equivalent weight of the sulfamic acid compound relative to the equivalent weight of bromine is preferably within a range from 0.5 to 1.5.

[0022]

5 In the ammoniacal nitrogen decomposers described above, the concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater is preferably 5 mg/L or greater.

ADVANTAGEOUS EFFECTS OF INVENTION

10 [0023]

The present invention enables the treatment of an ammoniacal nitrogen-containing wastewater using a simple method.

DESCRIPTION OF EMBODIMENTS

15 [0024]

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

[0025]

20 <Method for Treating Ammoniacal Nitrogen-Containing Wastewater>

The method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention is a method of incorporating a "bromine-based oxidizing agent" and a "sulfamic acid compound", or a method of incorporating a "reaction product of a bromine compound and a chlorine-based oxidizing agent" and a "sulfamic acid compound", in an ammoniacal nitrogen-containing wastewater that contains ammoniacal nitrogen. It is thought that this method produces a stabilized hypobromous acid composition in the ammoniacal nitrogen-containing wastewater.

[0026]

The method for treating an ammoniacal nitrogen-containing wastewater according to another embodiment of the present invention is a method of incorporating a stabilized hypobromous acid composition that is a "mixture of a bromine-based oxidizing agent and a sulfamic acid compound" or a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound", or a method of incorporating a stabilized hypobromous acid composition that is a "mixture of a sulfamic acid compound and a reaction product of a bromine compound and a chlorine-based oxidizing agent" or a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent", in an ammoniacal nitrogen-containing wastewater that contains ammoniacal nitrogen.

[0027]

Specifically, the method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention is a method of incorporating, for example, "bromine", "bromine chloride", "hypobromous acid" or a "reaction product of sodium bromide and hypochlorous acid", and a "sulfamic acid compound", in an ammoniacal nitrogen-containing wastewater.

[0028]

Furthermore, the method for treating an ammoniacal nitrogen-containing wastewater according to another embodiment of the present invention is a method of incorporating, for example, a stabilized hypobromous acid composition that is a "mixture of bromine and a sulfamic acid compound", a "mixture of bromine chloride and a sulfamic acid compound" or a "mixture of a sulfamic acid compound and a reaction product of sodium bromide and hypochlorous acid", in an ammoniacal nitrogen-containing wastewater. Further, the method for treating an ammoniacal nitrogen-containing wastewater according to another embodiment is a method of incorporating, for example, a stabilized hypobromous acid composition that is a "reaction product of bromine and a sulfamic acid compound", a "reaction product of bromine chloride and a sulfamic acid compound", or a "reaction

product of a sulfamic acid compound with a reaction product of sodium bromide and hypochlorous acid", in an ammoniacal nitrogen-containing wastewater.

[0029]

By using these methods, the ammoniacal nitrogen in the ammoniacal
5 nitrogen-containing wastewater can be effectively decomposed, and the ammoniacal
nitrogen-containing wastewater can be treated using a simple method. Further, these
methods enable an ammoniacal nitrogen-containing wastewater to be treated with a single
treatment agent. Furthermore, because a component is used that not only has the effect of
a disinfectant by reducing the coliform bacteria count (a disinfectant effect), but also has
10 the effect of decomposing ammoniacal nitrogen, the load on subsequent biological
treatments such as nitrification-denitrification processes can be reduced, enabling a more
advantageous wastewater treatment.

[0030]

The chlorine-based oxidizing agent sodium hypochlorite reacts with the ammoniacal
15 nitrogen in an ammoniacal nitrogen-containing wastewater to produce a combined halogen
(chloramine), resulting in a considerable reduction in the ammoniacal nitrogen
decomposition performance, but it is thought that the stabilized hypobromous acid
composition described above is able to directly decompose the ammoniacal nitrogen
without the intermediate formation of a combined halogen, and therefore compared with
20 chlorine-based oxidizing agents such as sodium hypochlorite, the ammoniacal nitrogen
decomposition effect is superior, and a more efficient treatment can be performed.
Further, it is thought that because the stabilized hypobromous acid composition described
above also contains a sulfamic acid compound, the ammoniacal nitrogen decomposition
effect is superior to that of hypobromous acid or salts thereof.

25 [0031]

In the method for treating an ammoniacal nitrogen-containing wastewater according
to an embodiment of the present invention, the "bromine-based oxidizing agent" or the
"reaction product of a bromine compound and a chlorine-based oxidizing agent", and the

"sulfamic acid compound" may be injected, using a chemical feed pump or the like, into the ammoniacal nitrogen-containing wastewater. The "bromine-based oxidizing agent" or the "reaction product of a bromine compound and a chlorine-based oxidizing agent", and the "sulfamic acid compound" may be added to the ammoniacal nitrogen-containing wastewater separately, or the neat liquids may be mixed together and then added to the ammoniacal nitrogen-containing wastewater as a mixture.

[0032]

Furthermore, for example, the "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" or the "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent" may be injected, using a chemical feed pump or the like, into the ammoniacal nitrogen-containing wastewater.

[0033]

The ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of "bromine" in the "bromine-based oxidizing agent" or the "reaction product of a bromine compound and a chlorine-based oxidizing agent", or the ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of "bromine", is preferably at least 0.1, more preferably within a range from 0.5 to 1.5, and even more preferably within a range from 1 to 1.5. Here, the ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of "bromine" represents the ratio of the value obtained by dividing the sulfamic acid compound content [wt%] within the stabilized hypobromous acid composition by the molecular weight of the sulfamic acid compound (97.1 when the sulfamic acid compound is sulfamic acid), relative to the value obtained by dividing the bromine content [wt%] in the stabilized hypobromous acid composition by the molecular weight of bromine (Br_2) (159.8). If the ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of "bromine" is less than 0.1, then a satisfactory ammoniacal nitrogen decomposition effect may not be obtainable, whereas if the ratio exceeds 1.5, then the production costs may

sometimes increase. Provided this equivalent weight ratio is within a range from 0.5 to 1.5, and more preferably within a range from 0.7 to 1.5, the ammoniacal nitrogen can be decomposed efficiently. Further, if this equivalent weight ratio is at least 1, then the stability of the formulation improves.

5 [0034]

The effective halogen concentration of the ammoniacal nitrogen-containing wastewater, calculated as an effective chlorine concentration, is preferably from 1 to 50 mg/L. If this concentration is less than 1 mg/L, then a satisfactory ammoniacal nitrogen decomposition effect may not be obtainable, whereas if the concentration exceeds 50 mg/L,
10 then corrosion of the piping or the like may occur.

[0035]

The ratio of the molar concentration of effective halogen, calculated as an effective chlorine concentration (the added molar concentration of the stabilized hypobromous acid composition), relative to the molar concentration of ammoniacal nitrogen ($\text{NH}_4\text{-N}$) in the
15 ammoniacal nitrogen-containing wastewater, is preferably at least 1.6, and more preferably 2.0 or greater. The larger this ratio becomes, the greater the ammoniacal nitrogen reduction effect may become.

[0036]

Examples of the bromine-based oxidizing agent include bromine (liquid bromine),
20 bromine chloride, bromic acid, bromate salts, and hypobromous acid and the like.

[0037]

Among these, compared with the formulation of "hypochlorous acid, a bromine compound and sulfamic acid" and the formulation of "bromine chloride and sulfamic acid" and the like, formulations that use bromine such as "bromine and a sulfamic acid
25 compound (a mixture of bromine and a sulfamic acid compound)" or a "reaction product of bromine and a sulfamic acid compound" tend to exhibit lower production of the by-product bromic acid, and are less likely to cause corrosion of metal materials such as supply pipes, and are consequently preferred.

[0038]

In other words, the method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention preferably involves incorporating bromine and a sulfamic acid compound (or incorporating a mixture of
5 bromine and a sulfamic acid compound) in the ammoniacal nitrogen-containing wastewater. Further, incorporating a reaction product of bromine and a sulfamic acid compound in the ammoniacal nitrogen-containing wastewater is also preferred.

[0039]

Examples of the bromine compound include sodium bromide, potassium bromide,
10 lithium bromide, ammonium bromide and hydrobromic acid. Among these, in terms of production costs and the like, sodium bromide is preferred.

[0040]

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

[0041]

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



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

[0042]

Examples of the sulfamic acid compound, in addition to sulfamic acid (amidosulfuric acid) in which the two R groups are both hydrogen atoms, include sulfamic acid compounds in which one of the two R groups is a hydrogen atom and the other is an

alkyl group having a carbon number of 1 to 8, such as N-methylsulfamic acid,

N-ethylsulfamic acid, N-propylsulfamic acid, N-isopropylsulfamic acid and

N-butylsulfamic acid, sulfamic acid compounds in which the two R groups are both alkyl groups having a carbon number of 1 to 8, such as N,N-dimethylsulfamic acid,

N,N-diethylsulfamic acid, N,N-dipropylsulfamic acid, N,N-dibutylsulfamic acid,

N-methyl-N-ethylsulfamic acid and N-methyl-N-propylsulfamic acid, and sulfamic acid

compounds in which one of the two R groups is a hydrogen atom and the other is an aryl group having a carbon number of 6 to 10, such as N-phenylsulfamic acid, as well as salts

of the above acids. Examples of the sulfamic acid salts include alkali metal salts such as sodium salts and potassium salts, alkaline earth metal salts such as calcium salts, strontium

salts and barium salts, other metal salts such as manganese salts, copper salts, zinc salts, iron salts, cobalt salts and nickel salts, as well as ammonium salts and guanidine salts.

One of these sulfamic acid compounds or salts may be used alone, or a combination of two or more compounds or salts may be used. In terms of the environmental burden and the like, the use of sulfamic acid (amidosulfuric acid) as the sulfamic acid compound is

preferred.

[0043]

In the method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention, an alkali is preferably also introduced.

Examples of the alkali include alkali hydroxides such as sodium hydroxide and potassium hydroxide. In terms of achieving good product stability and the like at low temperatures, a combination of sodium hydroxide and potassium hydroxide may also be used. The alkali is typically used not as a solid, but in the form of an aqueous solution.

5 [0044]

In the method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention, the pH of the ammoniacal nitrogen-containing wastewater that represents the treatment target is preferably within a range from 3 to 10, and more preferably from 4 to 9. If the pH of the ammoniacal nitrogen-containing
10 wastewater of the treatment target is less than 3, then the hypobromous acid is more likely to volatilize as bromine gas, and the decomposition effect on the ammoniacal nitrogen-containing wastewater may deteriorate, whereas if the pH is greater than 10, then the ammoniacal nitrogen is more likely to volatilize as ammonia gas and be lost, meaning the effectiveness of the treatment of the present invention may deteriorate.

15 [0045]

Examples of the ammoniacal nitrogen-containing wastewater that represents the treatment target of the method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention include workplace wastewater such as industrial wastewater from fish processing plants or the like, and sewage and the like.
20 The concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater that represents the treatment target is, for example, preferably at least 5 mg/L, and is more preferably within a range from 5 mg/L to 500 mg/L. The method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention can be applied favorably to the treatment of sewage and the like containing a
25 comparatively large amount of ammoniacal nitrogen of at least 5 mg/L. Further, for sewage and the like containing a comparatively large amount of ammoniacal nitrogen of at least 5 mg/L, a reduction in the coliform bacteria count can be achieved in addition to the decomposition effect on the ammoniacal nitrogen contained in the ammoniacal

nitrogen-containing wastewater. Particularly in those cases where a wastewater containing ammoniacal nitrogen is to be treated using a reverse osmosis membrane, if the pH of the wastewater is high, then a problem arises in that free ammonia can pass through the reverse osmosis membrane and leak into the permeate. However, by adding a stabilized hypobromous acid composition to the ammoniacal nitrogen-containing wastewater, as described in the method for treating an ammoniacal nitrogen-containing wastewater according to an embodiment of the present invention, thereby decomposing the ammoniacal nitrogen, and subsequently treating the resulting treated water having a reduced ammoniacal nitrogen content with the reverse osmosis membrane, the problem of leakage of free ammonia into the permeate can be suppressed.

[0046]

<Ammoniacal Nitrogen Decomposer>

An ammoniacal nitrogen decomposer according to an embodiment of the present invention contains a "bromine-based oxidizing agent", or a "reaction product of a bromine compound and a chlorine-based oxidizing agent", and a "sulfamic acid compound", and may also include an alkali.

[0047]

Further, an ammoniacal nitrogen decomposer according to another embodiment of the present invention contains a "mixture of a bromine-based oxidizing agent and a sulfamic acid compound" or a "mixture of a sulfamic acid compound and a reaction product of a bromine compound and a chlorine-based oxidizing agent", and may also include an alkali. Furthermore, an ammoniacal nitrogen decomposer according to another embodiment of the present invention contains a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" or a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent", and may also include an alkali.

[0048]

The bromine-based oxidizing agent, the bromine compound, the chlorine-based oxidizing agent, and the sulfamic acid compound are as described above.

[0049]

In terms of exhibiting little corrosion of metal materials such as piping, and yielding
5 lower production of the by-product bromic acid, decomposers containing bromine and a sulfamic acid compound (or containing a mixture of bromine and a sulfamic acid compound), such as a mixture of bromine, a sulfamic acid compound, an alkali and water, or decomposers containing a reaction product of bromine and a sulfamic acid compound, such as a mixture of a reaction product of bromine and a sulfamic acid compound, an alkali
10 and water are preferred as the ammoniacal nitrogen decomposer according to an embodiment of the present invention.

[0050]

It is thought that compared with chlorine-based oxidizing agents such as sodium hypochlorite, the ammoniacal nitrogen decomposer according to an embodiment of the
15 present invention is able to directly decompose the ammoniacal nitrogen without the intermediate formation of a combined halogen, and therefore exhibits a superior ammoniacal nitrogen decomposition effect. Further, it is thought that because the ammoniacal nitrogen decomposer according to an embodiment of the present invention contains a sulfamic acid compound, the ammoniacal nitrogen decomposition effect is
20 superior to that of hypobromous acid or salts thereof.

[0051]

The pH of the ammoniacal nitrogen decomposer typically exceeds 13.0, and is preferably 13.2 or higher. If the pH of the ammoniacal nitrogen decomposer is 13.0 or lower, then the effective halogen in the decomposer may sometimes become unstable.

25 [0052]

The bromate concentration in the ammoniacal nitrogen decomposer is preferably less than 5 mg/kg. If the bromate concentration in the ammoniacal nitrogen decomposer is 5 mg/kg or greater, then the concentration of bromate ions in the permeate may increase.

[0053]

<Method for Producing Ammoniacal Nitrogen Decomposer>

The ammoniacal nitrogen decomposer according to an embodiment of the present invention is obtained by mixing a bromine-based oxidizing agent and a sulfamic acid
5 compound, or by mixing a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound, and an alkali may also be mixed into the decomposer.

[0054]

The method for producing an ammoniacal nitrogen decomposer that contains
10 bromine and a sulfamic acid compound, or an ammoniacal nitrogen decomposer that contains a reaction product of bromine and a sulfamic acid compound preferably includes a step of adding and reacting bromine, under an inert gas atmosphere, with a mixed solution containing water, an alkali and a sulfamic acid compound, or a step of adding bromine,
under an inert gas atmosphere, to a mixed solution containing water, an alkali and a
15 sulfamic acid compound. By performing the addition and inducing the reaction under an inert gas atmosphere, or by performing the addition under an inert gas atmosphere, the bromate ion concentration in the decomposer can be reduced.

[0055]

Although there are no particular limitations on the inert gas used, at least one of
20 nitrogen and argon is preferred from a production perspective and the like, and nitrogen is particularly preferred in terms of production costs and the like.

[0056]

The oxygen concentration inside the reaction vessel during the bromine addition is preferably not more than 6 vol%, more preferably not more than 4 vol%, still more
25 preferably not more than 2 vol%, and most preferably 1 vol% or less. If the oxygen concentration inside the reaction vessel during the bromine reaction exceeds 6 vol%, then the amount of bromic acid produced in the reaction system may sometimes increase.

[0057]

The proportion of bromine added is preferably not more than 25 wt% relative to the total weight of the decomposer, and is more preferably at least 1 wt% but not more than 20 wt%. If the proportion of bromine added exceeds 25 wt% relative to the total weight of the decomposer, then the amount of bromic acid produced in the reaction system may sometimes increase. If the proportion is less than 1 wt%, then the ammoniacal nitrogen decomposition effect may be inferior.

[0058]

The reaction temperature during the bromine addition is preferably controlled within a range from at least 0°C to not more than 25°C, and in terms of production costs and the like, is more preferably controlled within a range from at least 0°C to not more than 15°C. If the reaction temperature during the bromine addition exceeds 25°C, then the amount of bromic acid produced in the reaction system may sometimes increase, whereas if the temperature is less than 0°C, then the reaction system may freeze.

EXAMPLES

[0059]

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

[0060]

<Preparation of Compositions>

Stabilized hypobromous acid compositions A, B, C-1, C-2, C-3 and C-4 and a hypobromite composition D used in the examples were as follows.

[0061]

[Preparation of Stabilized Hypobromous Acid Composition A]

Liquid bromine: 16.9 wt%, sulfamic acid: 10.7 wt%, sodium hydroxide: 12.9 wt%, potassium hydroxide: 3.94 wt% and water: the balance were mixed together under a nitrogen atmosphere to prepare a composition. The pH of the composition was 14, and

the bromine content was 16.9 wt%. A detailed description of the method for preparing the stabilized hypobromous acid composition A is presented below.

[0062]

A 2 liter four-necked flask into which nitrogen gas was injected continuously at a
5 flow rate controlled by a mass flow controller so that the oxygen concentration inside the reaction vessel was maintained at 1% was charged with 1,436 g of water and 361 g of sodium hydroxide, and following mixing, 300 g of sulfamic acid was added and mixed, and with the flask then cooled to maintain the temperature of the reaction solution at 0 to 15°C, 473 g of liquid bromine was added, and 230 g of a 48 wt% solution of potassium
10 hydroxide was then added, thus obtaining the target stabilized hypobromous acid composition A containing 10.7 wt% of sulfamic acid and 16.9 wt% of bromine relative to the total weight of the composition, and having a ratio for the equivalent weight of sulfamic acid relative to the equivalent weight of bromine of 1.04. Measurement of the pH of the prepared solution using the glass electrode method yielded a value of 14.
15 Measurement of the bromine content of the prepared solution using a method in which the bromine was substituted with iodine using potassium iodide, and a redox titration was then performed using sodium thiosulfate revealed a value of 16.9 wt%, which was 100.0% of the theoretical content (16.9 wt%). Further, the oxygen concentration inside the reaction vessel during the bromine reaction was measured using an "Oxygen Monitor JKO-02
20 LJDII" manufactured by Jikco Ltd. The bromate concentration was less than 5 mg/kg.

[0063]

The pH measurement was performed under the following conditions.

Electrode type: glass electrode

pH meter: IOL-30 model, manufactured by DKK-TOA Corporation

25 Electrode calibration: two-point calibration performed using the pH (6.86) of a neutral phosphate standard solution (type 2) manufactured by Kanto Chemical Co., Inc., and the pH (9.18) of a borate standard solution (type 2) manufactured by the same company.

Measurement temperature: 25°C

Measured value: the electrode was immersed in the liquid undergoing measurement, the value following stabilization was recorded as the measured value, and the average of three measurements was recorded

5 [0064]

[Preparation of Stabilized Hypobromous Acid Composition B]

The stabilized hypobromous acid composition B was prepared based on the content disclosed in WO 03/093171. The stabilized hypobromous acid composition B is a composition containing liquid bromine, a sulfamic acid salt and sodium hydroxide. The
10 pH of the stabilized hypobromous acid composition B was 14, the bromine content was 16.1 wt%, and the ratio of the equivalent weight of sulfamic acid relative to the equivalent weight of bromine was 1.45.

[0065]

[Preparation of Stabilized Hypobromous Acid Compositions C-1, C-2, C-3 and C-4]

15 These compositions were prepared using the procedure described below, based on the content disclosed in JP H11-506139 A. The pH of each composition was 14, and the bromine content was 11.3 wt%.

(1) First, 27.0 grams of a 40 wt% aqueous solution of sodium bromide was added to the weight of pure water shown in Table 1 and stirred.

20 (2) Subsequently, 41.7 g of a 12 wt% sodium hypochlorite solution was added to the solution from (1) and stirred.

(3) A stabilized aqueous solution including 56.0 g of pure water, 26.0 g of sulfamic acid and 18.0 g of sodium hydroxide was prepared.

(4) A weight of the stabilized solution from (3) shown in Table 1 was added to the
25 solution from (2) under stirring, thus obtaining the targeted stabilized hypobromous acid composition C-1, C-2, C-3 or C-4.

[0066]

[Table 1]

	Composition	Stabilized hypobromous acid composition C-1	Stabilized hypobromous acid composition C-2	Stabilized hypobromous acid composition C-3	Stabilized hypobromous acid composition C-4
Blend amount per 100 g of composition (g)	Pure water	28.7	23.5	18.2	13.0
	40 wt% aqueous solution of sodium bromide	27.0	27.0	27.0	27.0
	12% sodium hypochlorite	41.7	41.7	41.7	41.7
	Stabilized aqueous solution	2.6	7.8	13.1	18.3
pH of composition		13	13	13	13
Bromine content of composition [%]		11.3	11.3	11.3	11.3
Ratio of equivalent weight of sulfamic acid relative to the equivalent weight of bromine		0.1	0.3	0.5	0.7

[0067]

- 5 The ratio of the equivalent weight of sulfamic acid relative to the equivalent weight of bromine, for example in the stabilized hypobromous acid composition C-1, is calculated using the formula shown below.

$$\text{Ratio of equivalent weight of sulfamic acid relative to equivalent weight of bromine} = (2.6 \times 0.26 / 97.1) / (11.3 / 159.8) = 0.1$$

10 [0068]

[Preparation of Hypobromite Composition D]

This composition was prepared using the procedure described below. The pH of the hypobromite composition D was 12, and the bromine content was 11.3 wt%.

- (1) First, 27.0 g of a 40 wt% aqueous solution of sodium bromide was added to 31.3 g of pure water and stirred.

(2) Subsequently, 41.7 g of a 12 wt% sodium hypochlorite solution was added to the solution from (1) and stirred to obtain the hypobromite composition D.

[0069]

<Examples 1 to 3, Comparative Examples 1 and 2>

A simulated wastewater was prepared from Sagami-hara City water from which residual chlorine had been removed with activated carbon, by dissolving ammonium chloride in the water in an amount sufficient to generate an aqueous solution having an ammoniacal nitrogen ($\text{NH}_4\text{-N}$) concentration of 7.8 mg-N/L (0.56 mmol/L). The pH of the thus prepared simulated wastewater was 7.2. The stabilized hypobromous acid composition A (Example 1-1), the stabilized hypobromous acid composition B (Example 2), the stabilized hypobromous acid compositions C-1, C-2, C-3 and C-4 (Examples 3-1, 3-2, 3-3 and 3-4), the hypobromite composition D (Comparative Example 1) and sodium hypochlorite (Comparative Example 2) were each added to a sample of the prepared simulated wastewater in an amount sufficient to obtain an effective halogen concentration of 10 mg/L as Cl_2 , or the stabilized hypobromous acid composition A was added to a sample of the prepared simulated wastewater in an amount sufficient to obtain an effective halogen concentration of 1 mg/L as Cl_2 (Example 1-2). In each case, the change in the concentration of ammoniacal nitrogen ($\text{NH}_4\text{-N}$) over time (after 10 minutes, after 30 minutes) was measured while the test liquid was stirred at 500 rpm using a digital stirrer. After 30 minutes, the total halogen concentration of the test water was measured. The results are shown in Table 2.

[0070]

The total halogen concentration (effective equivalent chlorine concentration) was measured using the procedure described below.

[0071]

The effective halogen concentration refers to the value (mg/L as Cl_2) obtained by diluting the sample, and then performing measurement by the effective chlorine measurement method (namely, the DPD (diethyl-p-phenylenediamine) method), using a multipurpose water quality analyzer DR/4000 manufactured by Hach Company (wherein the measured item is "total chlorine"). The effective halogen concentration mentioned here is deemed to be the value obtained by measurement using the effective chlorine measurement method (DPD method). Further, the effective bromine concentration (mg/L

as Cl_2), reported as a chlorine-equivalent effective halogen concentration, can be calculated from the effective chlorine concentration, and is calculated as the measured value from the effective chlorine measurement method (DPD method) multiplied by 2.25 ($159.8 \text{ (g/mol)} / 70.9 \text{ (g/mol)}$) (wherein the molecular weight of chlorine (Cl_2) is 70.9 (g/mol) , and the

5 molecular weight of bromine (Br_2) is 159.8 (g/mol)).

[0072]

The ammoniacal nitrogen ($\text{NH}_4\text{-N}$) concentration (mg/L as N) was measured using the coloration principle of the indophenol blue absorptiometry method of JIS K 0102 42.2, using a PACKTEST (ammonium nitrogen, model: WAK- NH_4) from Kyoritsu

10 Chemical-Check Lab., Corp.

[0073]

[Table 2]

		Example 1-1	Example 1-2	Example 2	Example 3-1	Example 3-2	Example 3-3	Example 3-4	Comparative Example 1	Comparative Example 2
Added reagent		Stabilized hypobromous acid composition A	Stabilized hypobromous acid composition A	Stabilized hypobromous acid composition B	Stabilized hypobromous acid composition C-1	Stabilized hypobromous acid composition C-2	Stabilized hypobromous acid composition C-3	Stabilized hypobromous acid composition C-4	Hypobromite composition D	Sodium hypochlorite
Added concentration [mg/L as Cl ₂]		10	1	10	10	10	10	10	10	10
Ratio of equivalent weight of sulfamic acid relative to equivalent weight of bromine		1.04	1.04	1.45	0.10	0.30	0.50	0.70	0	—
NH ₄ -N concentration in simulated wastewater [mg/L]	Before treatment	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
	After 10 minutes	3.0	3.9	2.9	4.3	3.5	3.1	3.1	5.8	7.4
	After 30 minutes	2.5	3.6	2.5	3.8	3.4	3.0	2.6	5.6	7.2
Total halogen concentration in simulated wastewater [mg/L as Cl ₂]	After 30 minutes	3.7	0.9	3.8	2.7	2.6	2.8	3.4	2.3	7.8

[0074]

In Table 2, based on Comparative Example 2, it is evident that sodium hypochlorite is substantially unable to decompose ammoniacal nitrogen. It is thought that the reason for this is that the sodium hypochlorite reacts with the ammoniacal nitrogen in the wastewater to form combined halogen (chloramine), resulting in a marked reduction in the ammoniacal nitrogen decomposition performance. Further, based on Comparative Example 1, it is evident that even if a hypobromite is used, the ammoniacal nitrogen is unable to be satisfactorily decomposed. As is evident from Examples 1 to 3, when a stabilized hypobromous acid composition containing sulfamic acid was used, the ammoniacal nitrogen was able to be decomposed more effectively, and it was evident that the larger the ratio of the equivalent weight of sulfamic acid relative to the equivalent weight of bromine, the better the ammoniacal nitrogen reduction effect became. It was particularly clear that in those cases where the ratio of the equivalent weight of sulfamic acid relative to the equivalent weight of bromine in the stabilized hypobromous acid composition was 0.50 (Example 3-3) or 0.70 (Example 3-4) or greater, a superior ammoniacal nitrogen reduction effect was obtained. Further, based on a comparison of Example 1-2 and Comparative Examples 1 and 2, it was clear that the stabilized hypobromous acid composition A yielded a superior ammoniacal nitrogen decomposition effect even when added at a low concentration.

[0075]

<Examples 1-3 to 1-7>

A simulated wastewater was prepared from Sagamihara City water from which residual chlorine had been removed with activated carbon, by dissolving ammonium chloride in the water in an amount sufficient to generate an aqueous solution having an ammoniacal nitrogen ($\text{NH}_4\text{-N}$) concentration of 7.8 mg-N/L (0.56 mmol/L). The pH of the thus prepared simulated wastewater was 7.2. The stabilized hypobromous acid composition A (Examples 1-3 to 1-7) was added to the prepared simulated wastewater in an amount sufficient to obtain an effective halogen concentration of 15 mg/L as Cl_2 (0.21

mmol/L) (Example 1-3), 40 mg/L as Cl₂ (0.56 mmol/L) (Example 1-4), 61 mg/L as Cl₂ (0.87 mmol/L) (Example 1-5), 79 mg/L as Cl₂ (1.11 mmol/L) (Example 1-6), or 99 mg/L as Cl₂ (1.40 mmol/L) (Example 1-7). In each example, the change in the concentration of ammoniacal nitrogen (NH₄-N) over time (after 10 minutes, after 30 minutes) was measured while the test liquid was stirred at 500 rpm using a digital stirrer. After 30 minutes, the total halogen concentration of the test water was measured. The results are shown in Table 3. The total halogen concentration (effective equivalent chlorine concentration) and the ammoniacal nitrogen (NH₄-N) concentration (mg/L as N) were measured using the methods described above.

10 [0076]

In Table 3, it was evident that the greater the ratio of the molar concentration of effective halogen (calculated as an effective chlorine concentration) (namely, the added molar concentration of the stabilized hypobromous acid composition) relative to the molar concentration (0.56 mmol/L) of ammoniacal nitrogen (NH₄-N) in the simulated water prior to treatment, the greater the ammoniacal nitrogen reduction effect became. In particular, it was evident that when the ratio of the molar concentration of effective halogen (calculated as an effective chlorine concentration) (the added molar concentration of the stabilized hypobromous acid composition) relative to the molar concentration of ammoniacal nitrogen (NH₄-N) in the simulated water prior to treatment was 1.6 (Example 1-5) or greater, the ammoniacal nitrogen was able to be almost completely decomposed.

[0077]

[Table 3]

		Example 1-3	Example 1-4	Example 1-5	Example 1-6	Example 1-7
Added reagent		Stabilized hypobromous acid composition A				
Added reagent concentration	[mg/L as Cl ₂]	15	40	61	79	99
	[mmol/L as Cl ₂]	0.21	0.56	0.87	1.11	1.40
NH ₄ -N concentration in simulated wastewater	[mg/L]	7.8				
	[mmol/L]	0.56				
Ratio of added reagent molar concentration relative to NH ₄ -N molar concentration in simulated wastewater		0.4	1.0	1.6	2.0	2.5
NH ₄ -N concentration in simulated wastewater [mg/L]	Before treatment	7.8	7.8	7.8	7.8	7.8
	After 10 minutes	2.9	2.3	0.9	0	0
	After 30 minutes	2.5	2.2	0.8	0	0
Total halogen concentration in simulated wastewater [mg/L as Cl ₂]	After 30 minutes	3.9	4.4	4.5	14.5	32.0

[0078]

5 <Example 4>

Using a sewage containing ammoniacal nitrogen and having the water quality shown in Table 4, an evaluation test of the ammoniacal nitrogen decomposition performance and the disinfecting performance of a stabilized hypobromous acid composition was performed. The reagent (the stabilized hypobromous acid composition A) was added to a 300 mL beaker in an amount sufficient to obtain an effective halogen concentration of 5 mg/L as Cl₂, and the mixture was stirred with a digital stirrer at 250 rpm. Three minutes after addition of the reagent, a prescribed amount of the treated water was sampled, the ammoniacal nitrogen (NH₄-N) concentration was measured, and following the addition of sodium thiosulfate to inactivate the effective chlorine, a coliform bacteria count measurement was performed using a Petrifilm CC plate.

[0079]

[Table 4]

Analysis item	Measured value (before reagent addition)	Measured value (3 minutes after reagent addition)
NH ₄ -N concentration [mg/L]	15	5
Coliform bacteria count [/mL]	100,000	43

[0080]

- 5 Table 4 confirmed that the stabilized hypobromous acid composition exhibited a reduction effect on the coliform bacteria count as well as an ammoniacal nitrogen decomposition effect, even for sewage or the like containing a comparatively large amount of ammoniacal nitrogen.

CLAIMS

1. A method for treating an ammoniacal nitrogen-containing wastewater, the method comprising incorporating
5 a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and
a sulfamic acid compound
in an ammoniacal nitrogen-containing wastewater containing ammoniacal nitrogen;
wherein a ratio of an equivalent weight of the sulfamic acid compound relative to an
10 equivalent weight of bromine is within a range from 0.5 to 1.5; and
wherein a ratio of a molar concentration of effective halogen, calculated as an effective chlorine concentration, relative to a molar concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater, is 1.6 or greater.
- 15 2. A method for treating an ammoniacal nitrogen-containing wastewater, the method comprising incorporating a mixture or a reaction product of
a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and
a sulfamic acid compound in an ammoniacal nitrogen-containing wastewater
20 containing ammoniacal nitrogen;
wherein a ratio of an equivalent weight of the sulfamic acid compound relative to an equivalent weight of bromine is within a range from 0.5 to 1.5; and
wherein a ratio of a molar concentration of effective halogen, calculated as an effective chlorine concentration, relative to a molar concentration of ammoniacal nitrogen
25 in the ammoniacal nitrogen-containing wastewater, is 1.6 or greater.
3. A method for treating an ammoniacal nitrogen-containing wastewater, the method comprising

incorporating a mixture of bromine and a sulfamic acid compound, or
incorporating a reaction product of bromine and a sulfamic acid compound,
in an ammoniacal nitrogen-containing wastewater containing ammoniacal nitrogen;
wherein a ratio of an equivalent weight of the sulfamic acid compound relative to an
5 equivalent weight of bromine is within a range from 0.5 to 1.5; and
wherein a ratio of a molar concentration of effective halogen, calculated as an
effective chlorine concentration, relative to a molar concentration of ammoniacal nitrogen
in the ammoniacal nitrogen-containing wastewater, is 1.6 or greater.

10 4. The method for treating an ammoniacal nitrogen-containing wastewater according to
Claim 1, wherein

after incorporating the bromine-based oxidizing agent, or the reaction product of a
bromine compound and a chlorine-based oxidizing agent, and the sulfamic acid compound,
in the ammoniacal nitrogen-containing wastewater, a treated water containing a reduced
15 amount of ammoniacal nitrogen is further treated with a reverse osmosis membrane.

5. The method for treating an ammoniacal nitrogen-containing wastewater according to
Claim 2, wherein

after incorporating the mixture or the reaction product of the bromine-based
20 oxidizing agent, or the reaction product of a bromine compound and a chlorine-based
oxidizing agent, and the sulfamic acid compound, in the ammoniacal nitrogen-containing
wastewater, a treated water containing a reduced amount of ammoniacal nitrogen is further
treated with a reverse osmosis membrane.

25 6. The method for treating an ammoniacal nitrogen-containing wastewater according to
Claim 3, wherein

after incorporating the mixture of bromine and the sulfamic acid compound, or after
incorporating the reaction product of bromine and the sulfamic acid compound, in the

ammoniacal nitrogen-containing wastewater, a treated water containing a reduced amount of ammoniacal nitrogen is further treated with a reverse osmosis membrane.

7. The method for treating an ammoniacal nitrogen-containing wastewater according to any one of Claims 1 to 6, wherein

a concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater is 5 mg/L or greater.

8. An ammoniacal nitrogen decomposer for decomposing ammoniacal nitrogen in an ammoniacal nitrogen-containing wastewater, wherein the ammoniacal nitrogen decomposer comprises either

(a) a mixture of bromine and a sulfamic acid compound, or

(b) a reaction product of (i) bromine and (ii) a sulfamic acid compound;

wherein a ratio of an equivalent weight of the sulfamic acid compound relative to an equivalent weight of bromine is within a range from 0.5 to 1.5; and

wherein a ratio of a molar concentration of effective halogen, calculated as an effective chlorine concentration, relative to a molar concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater, is 1.6 or greater.

9. The ammoniacal nitrogen decomposer according to Claim 8, wherein

a concentration of ammoniacal nitrogen in the ammoniacal nitrogen-containing wastewater is 5 mg/L or greater.