

METHOD FOR STERILIZING WATER SYSTEM

Technical Field

[0001]

The present invention relates to a method for sterilizing a water system. More particularly, the present invention relates to a sterilization technique using free chlorine and combined chlorine when a water system is sterilized.

Background Art

[0002]

In a plant cooling water system in various factories, a treated wastewater system, an iron and steel wastewater system, a pulp and paper wastewater system, a cutting oil wastewater system, or the like, bacteria, filamentous fungi, algae, or the like cause slime in the water system. The slime causes troubles such as poor thermal efficiency, blockage of water piping, and corrosion of piping metal.

[0003]

In order to prevent such troubles, a method using pharmaceutical agents is used for sterilizing the water systems. As the sterilization method, an oxidizing agent such as a hypochlorite is conventionally used because of its good sterilization effect at low cost. However, when the hypochlorite or the like is used at a concentration effective for peeling the slime, a metal member in the water system is corroded.

[0004]

Meanwhile, as the technique also relating to the inhibition of the

corrosion in the water system, the applicants have already provided a slime peeling agent and the like that include a chlorine-based oxidizing agent containing sulfamic acid or a salt thereof and an alkali (see Patent Document 1). Furthermore, the applicants have also provided an antimicrobial algicidal agent composition and the like that include a chlorine-based oxidizing agent containing an azole-based compound and sulfamic acid or a salt thereof (see Patent Document 2).

[0005]

By at least combining a chlorine-based oxidizing agent and sulfamic acid, a treatment having stable slime peelability and low corrosivity can be carried out. These techniques previously provided by the applicants can produce excellent effects. However, as the sterilization techniques for the water system, more excellent techniques are required to be developed in various industrial circles.

[0006]

[Patent Document 1] Japanese Patent No. 3915560.

[Patent Document 2] Japanese Patent No. 3832399.

Disclosure of the Invention

Technical Problems to be Solved

[0007]

The chlorine-based oxidizing agent is used as a strong oxidizing agent for sterilization treatment and the like. However, it has problems such as poor control due to its high decomposition rate and high corrosivity. Furthermore, it has another problem in which, when slime structure is

formed on walls or the like of a water system plant or the like, oxidation reaction occurs on the surface of the slime structure and thus the deep part is difficult to be sterilized.

[0008]

Therefore, it is a main object of the present invention to provide a method for sterilizing a water system by which the sterilization and the slime control can be efficiently carried out in a water system.

Summary

[0008a]

In one aspect, there is provided a method for sterilizing legionella bacteria in a water system comprising:

making combined chlorine and free chlorine present in the water system; and

keeping a concentration of the free chlorine in the water system at 0.3 to 0.8 mg-Cl/L by measuring free chlorine concentration of the water system and controlling the amount of free chlorine based on the measured value.

Means to Solve the Problems

[0009]

First, the present invention provides a method for sterilizing a water system that includes making combined chlorine and free chlorine present in the water system, and keeping a concentration of the free chlorine in the water system at 0.3 mg-Cl/L or higher. When the combined chlorine and the free chlorine are made to be present in a water system and the concentration of the free chlorine is kept at 0.3 mg-Cl/L or higher, the sterilizability and the like of the combined chlorine can be further improved.

In addition, the combined chlorine is capable of being formed by adding at least a chlorine-based oxidizing agent and a sulfamic acid

compound into the water system. When the chlorine-based oxidizing agent and the sulfamic acid compound are used, a chlorosulfamic acid compound can be formed as the combined chlorine.

Furthermore, the free chlorine is capable of being formed by adding at least one of a hypochlorite, a chlorite, chlorine dioxide, and chlorine gas into the water system.

Effect of the Invention

[0010]

According to the sterilization method pertaining to the present invention, the sterilization and the slime control can be efficiently carried out in a water system.

Best Mode for Carrying Out the Invention

[0011]

Hereinafter, the present invention will be described. The below description shows typical embodiments of the present invention and does not intend to limit the scope of the invention.

[0012]

The sterilization method of the present invention is carried out at least by making combined chlorine and free chlorine present in a water system and keeping the concentration of the free chlorine at 0.3 mg-Cl/L or higher. The presence of the combined chlorine and the free chlorine in a water system can peel a slime structure formed on the surfaces and the like of various members in the water system and can efficiently sterilize dispersed microorganisms and the like. In addition, it can decrease the decomposition rate as the sterilizing agent and can reduce the corrosivity.

[0013]

In the invention, the combined chlorine and the free chlorine are simply present in water to be treated as the treatment target, and the existence forms are not limited. When at least the free chlorine is remained at a certain concentration or higher in a water system, the sterilizability of the combined chlorine can be improved. Hereinafter, it will be described in detail.

[0014]

The type of the combined chlorine is not limited and examples thereof include chloramine-T (a sodium salt of N-chloro-4-methylbenzenesulfonamide), chloramine-B (a sodium salt of N-chlorobenzenesulfonamide), a sodium salt of N-chloro-para-nitrobenzenesulfonamide, trichloromelamine, a sodium salt or a potassium salt of mono- or di-chloromelamine, a trichloroisocyanurate, a sodium salt or a potassium salt of mono- or di-chloroisocyanuric acid, a sodium salt or a potassium salt of mono- or di-chlorosulfamic acid, and monochlorohydantoin or 1,3-dichlorohydantoin or a 5,5-alkyl derivative thereof.

[0015]

The combined chlorine may be added into the water system or may be formed in the water system. For example, a chlorine-based oxidizing agent and a sulfamic acid compound may be added in the water system to form a chlorosulfamic acid compound or the like. When the chlorine-based oxidizing agent and the sulfamic acid compound or a chlorosulfamic acid-based combined chlorine agent formed from the chlorine-based oxidizing agent and the sulfamic acid compound is added into water to be treated, there is a feature that the concentration of the free chlorine in the water to be treated does not largely vary in a wide pH range from an acidic region to an alkaline region.

[0016]

The sulfamic acid compound used in the invention is not specifically limited and examples thereof include sulfamic acid and a salt thereof.

Specifically, sulfamic acid, ammonium sulfamate, and the like may be used. The sulfamic acid compounds are not poisonous like hydrazine and are highly safe.

[0017]

Examples of such sulfamic acid compound include N-methylsulfamic acid, N,N-dimethylsulfamic acid, and N-phenylsulfamic acid. Among the sulfamic acid compounds used in the invention, examples of the salt of the compound include alkali metal salts such as a sodium salt and a potassium salt, alkaline earth metal salts such as a calcium salt, a strontium salt, and a barium salt, other metal salts such as a manganese salt, a copper salt, a zinc salt, an iron salt, a cobalt salt, and a nickel salt, an ammonium salt, and a guanidine salt. Specific examples thereof include sodium sulfamate, potassium sulfamate, calcium sulfamate, strontium sulfamate, barium sulfamate, iron sulfamate, and zinc sulfamate. The sulfamic acid and the salt of the sulfamic acid may be used alone or in combination of two or more.

[0018]

The chlorine-based oxidizing agent used in the invention is not specifically limited and examples thereof include chlorine gas, chlorine dioxide, hypochlorous acid or a salt thereof, chlorous acid or a salt thereof, chloric acid or a salt thereof, perchloric acid or a salt thereof, and chlorinated isocyanuric acid or a salt thereof.

[0019]

More specific examples of the salt 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 of chlorous acid such as calcium chlorite and barium chlorite, other metal salts of chlorous acid such as nickel chlorite, ammonium chlorate, alkali metal salts of chloric acid such as sodium chlorate and potassium chlorate, and alkaline earth metal salts of chloric acid such as calcium chlorate and barium chlorate.

[0020]

These chlorine-based oxidizing agents may be used alone or in combination of two or more. Among them, the hypochlorites are suitably used because of the easy handling.

[0021]

The concentration of the combined chlorine in the water system is not limited. The lower limit is preferably 1.0 mg-Cl/L or higher and the upper limit is preferably 20 mg-Cl/L or lower. In the present invention, the concentration of the combined chlorine is measured according to the DPD (N,N-diethylphenylenediamine) method described in Japanese Industrial Standard K 0102. When the combined chlorine concentration is kept in such range, the amount of the free chlorine in the water system can be controlled with higher precision. Thus, the sterilization and the slime control can be further efficiently carried out, and also the decomposition rate can be made to be lower. As a result, the bactericidal activity can be maintained over a long term.

[0022]

The method for making the free chlorine present in the water system is not limited. Examples thereof include a method of adding an agent such

as a hypochlorite, a chlorite, chlorine dioxide, and chlorine gas into the water system and a method of generating hypochlorite ions using an electrolytic reaction of a salt solution, an aqueous solution of potassium chloride, or the like.

[0023]

It is desirable that the concentration of the free chlorine in the water system is 0.3 mg-Cl/L or higher, preferably 0.4 mg-Cl/L or higher, and more preferably 0.5 mg-Cl/L or higher. When the free chlorine concentration is kept in such range, the sterilization and the slime control can be further efficiently carried out and the decomposition rate can be made to be lower. As a result, the bactericidal activity can be maintained over a long term.

[0024]

Examples of the method of measuring the concentration of the free chlorine in the water system include polarography, absorptiometry, and a method in which an oxidation-reduction potential (ORP) in the water system is measured to estimate the free chlorine concentration based on the oxidation-reduction potential. In the present invention, the concentration of the chlorine is measured according to the DPD method described in Japanese Industrial Standard K 0102. Based on the free chlorine concentration obtained in this manner, the amount of the free chlorine can be controlled so as to be a target concentration of the free chlorine.

[0025]

In the present invention, the free chlorine concentration in the water system may be measured as necessary to control the amount of the free chlorine in the water system based on the measured value. Namely, control

means in which the concentration of the free chlorine in the water system is measured to control the amount of the free chlorine in the water system based on the measured value may be separately arranged. Consequently, the water quality can be continuously managed in the water system. The control means is not specifically limited and, for example, the amount of the free chlorine can be controlled by adding an agent or the like based on the measured concentration of the chlorine.

[0026]

Furthermore, when the combined chlorine concentration in a water system is also required to be controlled, the combined chlorine concentration in the water system may be also measured to control the amount of the combined chlorine in the water system based on both of the measured free chlorine concentration and the measured combined chlorine concentration. When not only the free chlorine concentration but the combined chlorine concentration are monitored, the water quality can be continuously managed with higher precision.

[0027]

The action mechanism of the sterilization method of the present invention is supposed that the combined chlorine peels or disperses the slime structure from the surface of a member and the like and then the free chlorine sterilizes the dispersed pathogens and the like. Accordingly, the sterilization and the slime control can be efficiently carried out. The knowledge is only based on the expectation. Thus, even when the sterilization is carried out by any action and the like other than the knowledge, it is, of course, included in the scope of the invention.

[0028]

Treatment objects applicable with the sterilization method of the present invention are not specifically limited. Examples thereof include a plant cooling water system in various factories, a scrubber, a wastewater effluent system, a treated wastewater system, an iron and steel wastewater system, and a cutting oil wastewater system. The slime structure adhered on the apparatus, water piping, and the like can be peeled.

[0029]

As the water system, a circulating water system where the slime structure is especially readily generated is suitably applied to and an open circulating cooling water system and the like are specifically suitable. For example, bacteria such as Legionella bacteria prefer the water temperature of an open circulating cooling tower and the like, specifically prefer the environment surrounded by algae grown in the cooling tower, and are readily grown in the water system under such condition. According to the present invention, the effective bactericidal activity can be maintained especially in the open circulating cooling water system and the like over a long term.

Examples

[0030]

Hereinafter, the present invention will be described more specifically with reference to examples, and the effect of the invention will be examined.

[0031]

[Example 1]

Cooling water for air conditioning contaminated with Legionella

bacteria was sterilized with chlorosulfamic acid and free chlorine. The free chlorine was controlled by adding a hypochlorite.

The cooling tower had a refrigeration capacity of 300 RT and a holding water quantity of 30 m³ and was run at a concentration rate of 5 times. The chlorosulfamic acid was added at a ratio of 15 mg/L to the amount of blow water from the cooling water.

The peeled slime was naturally exhausted by the blow depending on the concentration, and particular removal such as cleaning was not carried out.

The free chlorine was managed by that the residual chlorine concentration was measured according to the DPD method to control the addition amount of the agent. The free chlorine concentration was measured with a residual chlorine analyzer "Cl-17 (manufactured by HACH Company)". The number of Legionella bacteria in the treated water was evaluated by the colony forming units (CFU) in 100 mL of the treated water.

As a result, when the free chlorine concentration was 0.2 mg-Cl/L, the number of Legionella bacteria was decreased but the non-detection could not be maintained. However, when the free chlorine concentration was managed at 0.3 mg-Cl/L or higher, the non-detection of the number of Legionella bacteria could be maintained. In particular, when the free chlorine concentration was managed at 0.4 mg-Cl/L or higher after two months or later, the occurrence of Legionella bacteria was completely inhibited (Fig. 1).

[0032]

[Comparative Example 1]

The test was carried out in the similar condition as in Example 1 except that only the chlorosulfamic acid was used for the treatment. As a result, the free chlorine concentration had not been more than 0.1 mg-Cl/L, the number of Legionella bacteria had once disappeared but then occurred again (Fig. 2).

[0033]

[Discussion]

The above results shows that, when the combined chlorine and the free chlorine are made to be present in the water system and the concentration of the free chlorine in a water system is kept at least at 0.3 mg-Cl/L or higher, the sterilization and the slime control can be efficiently carried out.

Brief Description of Drawings

[0034]

[Fig. 1] Fig. 1 is a graph showing the relation between the free chlorine concentration, the number of Legionella bacteria, and the treatment period when two agents were used for the treatment.

[Fig. 2] Fig. 2 is a graph showing the relation between the free chlorine concentration, the number of Legionella bacteria, and the treatment period when only one agent was used for the treatment.

CLAIMS:

1. A method for sterilizing legionella bacteria in a water system comprising:
 - making combined chlorine and free chlorine present in the water system; and
 - keeping a concentration of the free chlorine in the water system at 0.3 to 0.8 mg-Cl/L by measuring free chlorine concentration of the water system and controlling the amount of free chlorine based on the measured value.
2. The method for sterilizing legionella bacteria in a water system according to claim 1, wherein the free chlorine is formed by adding at least one of hypochlorite, chlorite, chlorine dioxide, and chlorine gas into the water system; and controlling the amount of free chlorine in the water system by adjusting amount of chemical feed of the hypochlorite, the chlorite, the chlorine dioxide, and/or the chlorine gas based on a residual chlorine concentration in the water system.
3. The method for sterilizing legionella bacteria in a water system according to claim 1 or 2, wherein the combined chlorine is formed by adding at least a chlorine-based oxidizing agent and a sulfamic acid compound into the water system; and measuring combined chlorine concentration of the water system, and adjusting the combined chlorine concentration in the water system based on both the free chlorine concentration and the combined chlorine concentration.