

10-249392

(43) Publication Date September 22, 1998

(51) Int. Cl.⁶

C02F 3/34

3/12

Identification Code

101

ZAB

ZAB

FI

C02F 3/34

3/12

101A

ZABZ

V

ZABD

Examination Request: not yet made Number of Claims: 5 FD (Total 13 pages)

(21) Application No.: 9-76499

(22) Application Date: March 12, 1997

(71) Applicant: 000006208
Mitsubishi Heavy Industries, Ltd.
2-5-1 Marunouchi, Chiyoda-ku, Tokyo-to
000217686(71) Applicant: Electric Power Development Co., Ltd.
6-15-1 Ginza, Chuou-ku, Tokyo-to(72) Inventor: OKAZOE, Kiyoshi
Mitsubishi Heavy Industries, Ltd.
2-5-1 Marunouchi, Chiyoda-ku, Tokyo-to(72) Inventor: OCHI, Eiji
Mitsubishi Heavy Industries, Ltd.
2-5-1 Marunouchi, Chiyoda-ku, Tokyo-to
(74) Agent: Patent Attorney, MIURA, Yoshikazu

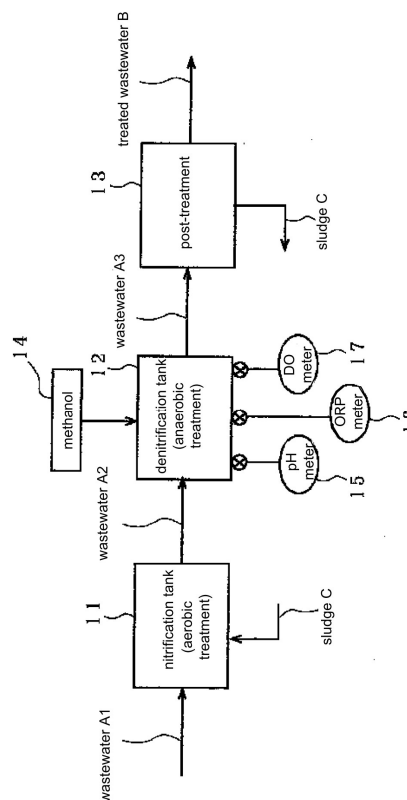
Continued on the last page

(54) Title of the Invention: Wastewater Treatment Method

(57) [Abstract]

[Problem to Be Solved] To provide a wastewater treatment method that can effectively remove nitrogen and selenium (particularly hexavalent selenium) in wastewater and achieve compliance with a selenium leaching standard or the like at a low cost, wherein the wastewater treatment method allows a very efficient selenium removal treatment by setting treatment conditions.

[Means for Solving the Problem] A wastewater treatment method that removes at least nitrogen and hexavalent selenium from wastewater containing nitrogen and selenium by way of a microbial treatment that uses an activated sludge containing at least a microorganism having the ability to denitrify and a microorganism having the ability to reduce selenium that reduces hexavalent selenium to tetravalent selenium and/or elementary selenium, wherein organic matter that is the nutrient source for microorganisms in the activated sludge is added to a treatment tank in which the microbial treatment is implemented within a range exceeding the denitrification equivalent by 5 mg/liter-h or more.



[Claims]

[Claim 1] A wastewater treatment method that removes at least nitrogen and hexavalent selenium from wastewater that contains nitrogen and selenium by a microbial treatment that uses an activated sludge containing at least a microorganism having the ability to denitrify and a microorganism having the ability to reduce selenium that reduces hexavalent selenium to tetravalent selenium and/or elementary selenium, characterized in that organic matter that is the nutrient source for microorganisms in the activated sludge is added to a treatment tank in which the microbial treatment is implemented within a range exceeding the denitrification equivalent by 5 mg/liter·h or more.

[Claim 2] The wastewater treatment method according to claim 1, characterized in that a selenate reducing bacterium FERM BP-5661 belonging to the genus *Pseudomonas* is used as the microorganism having the ability to reduce selenium.

[Claim 3] The wastewater treatment method according to claim 1 or 2, characterized in that the oxidation-reduction potential in the treatment tank in which the microbial treatment is implemented is maintained to be no more than 300 mV.

[Claim 4] The wastewater treatment method according to claim 1 or 2 characterized in that the oxidation-reduction potential in the treatment tank in which the microbial treatment is implemented is maintained in a range of no less than -200 mV to no more than 200 mV.

[Claim 5] The wastewater treatment method according to any of claims 1 to 4 characterized in that the concentration of nitrogen flowing into the treatment tank in which the microbial treatment is implemented is detected, and the dose of organic matter is adjusted on the basis of the detected value, so as to be within said range.

[Detailed Description of the Invention]**[0001]**

[Technical Field of the Invention] The present invention relates to a wastewater treatment method that can effectively remove nitrogen along with selenium (particularly hexavalent selenium) in wastewater.

[0002]

[Prior Art] Because selenium has a toxicity similar to arsenic compounds and there have been cases of harm and restrictions on emissions in other countries, Japan also newly added selenium to its regulations in February 1994 and established an environmental standard (0.01 mg/liter), an emissions standard (0.1 mg/liter), and a leaching standard for landfill disposal (0.3 mg/liter). Furthermore, selenium is present in wastewater as tetravalent selenium (principal form: selenite SeO_3^{2-}) and hexavalent selenium (principal form: selenate SeO_4^{2-}), and hexavalent selenium in particular is readily eluted as it has a high solubility (95% solubility at 20°C).

[0003] Furthermore, a method for removing tetravalent selenium contained in conventional wastewater or the like by way of insolubilization by FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ and a chelating agent (for example EPOLAS MX-7, a Miyoshi Resin product) or a heavy metal scavenging polymer agent (for example EPOFLOC L-1, a Miyoshi Resin product) and solid-liquid separation can be considered. However, an effective method for conventional hexavalent selenium has not been discovered. For this reason, conventionally there was a problem of requiring a costly and cumbersome treatment, for example desulfurization wastewater or the like, is diluted with a large volume of water, when wastewater contained selenium (particularly hexavalent selenium) in order to comply with the leaching standard or the like.

[0004]

[Problems to Be Solved by the Invention] Here, the applicants proposed a wastewater treatment method that uses

a hexavalent selenium reduction treatment by microorganisms in Japanese patent application No. 7-292706. This method is described below using FIG. 6. In FIG. 6, a desulfurization device 1 absorbs and removes sulfur oxides in flue gas by bringing the flue gas in contact with an absorption liquid in which limestone is suspended, for example, and a substantial amount of selenium from the flue gas is dissolved into this wastewater A. The wastewater from a typical desulfurization device contains approximately 0.3 mg/liter of hexavalent selenium and, after the hexavalent selenium is reduced to tetravalent selenium and/or elementary selenium in a downstream wastewater treatment device 2, is discharged as treated wastewater B after a step of removing tetravalent selenium.

[0005] Here, a coagulation settling step is a step of removing, with a coagulation sedimentation device, fine solids (particles) that were not separated in a solid-liquid separation treatment for collecting gypsum in the desulfurization device 1, and a COD treatment step is a step of removing inorganic pollutants in order to reduce the COD value to be no more than a reference value. This COD treatment step can be performed with a method that thermally decomposes pollutants by boiling the wastewater at a high temperature, or with a well-known method that selectively adsorbs specific pollutants with an adsorption resin. Note that all or a portion of the tetravalent selenium contained in wastewater is removed by reacting with a coagulant in the coagulation settling treatment to become selenite and precipitate on the solid-phase side, but the hexavalent selenium, at least, is discharged to the downstream side still dissolved in the wastewater even with the coagulation settling step and the COD treatment step.

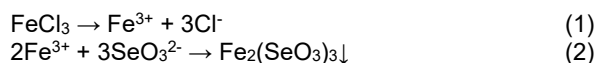
[0006] In a microbial treatment step, an aerobic treatment (aerobic microbial treatment), an anaerobic treatment (anaerobic microbial treatment), and a settling treatment (solid-liquid separation) are each performed in order. In the aerobic treatment here, activated sludge containing ammonia-oxidizing bacteria (bacteria having the property of producing NO_2^- by oxidizing NH_4^+) and nitrite-oxidizing bacteria (bacteria having the property of producing NO_3^- by oxidizing NO_2^-) is used, wastewater after the COD treatment step is introduced and mixed in a stirring tank in which the activated sludge is floating or suspended, and aeration (exposure to air) is performed as necessary by blowing.

[0007] In the aerobic treatment, after a suitable residence time, the NH_4^+ in the wastewater becomes NO_2^- that has been oxidized by the ammonia-oxidizing bacteria in the activated sludge, and then the NO_2^- becomes NO_3^- that has been oxidized by the nitrite-oxidizing bacteria in the activated sludge. Note that wastewater that has completed the aerobic treatment is sent to the downstream side (stirring tank or the like during anaerobic treatment described below) in a state in which as little of the activated sludge used in the aerobic treatment as possible is present, by performing settling treatment or the like as required.

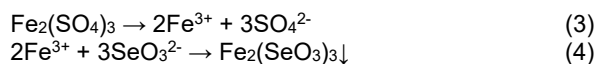
[0008] Next, the anaerobic treatment uses activated sludge containing microorganisms having the ability to reduce selenium, which reduce hexavalent selenium to tetravalent selenium and/or elementary selenium, and denitrifying bacteria (bacteria having the ability to produce N_2 by reducing NO_3^-),

introduces and mixes wastewater, after the aerobic treatment, in the stirring tank in which the activated sludge is floating or suspended, and maintains an anaerobic environment while supplying nutrition such as methanol. In this anaerobic treatment, after a suitable residence time, NO_3^- in the wastewater becomes N_2 by being reduced by the denitrifying bacteria in the activated sludge and the hexavalent selenium (principal form: selenate SeO_4^{2-}) in the wastewater is simultaneously reduced to tetravalent selenium (principal form: selenite SeO_3^{2-}) by microorganisms having the ability to reduce selenium or further becomes elementary selenium.

[0009] In addition, in the settling treatment, wastewater after the anaerobic treatment is sent downstream (step of removing tetravalent selenium) after being introduced into a sedimentation separation device or the like and having the sludge (solids) removed, for example. In this case, because elementary selenium solubility is extremely low, it precipitates almost entirely as a solid, and because the solubility of tetravalent selenium is low compared to hexavalent selenium, some also precipitates. Thus,



or



[0012] Thus, in the next coagulation settling treatment, when the wastewater is separated into solid and liquid by a coagulation sedimentation device or the like, the tetravalent selenium is separated to the solid-phase side as ferric selenite and is incorporated into the discharged solids (sludge) by being made insoluble. Accordingly, the treated wastewater B discharged from the wastewater treatment device 2 contains almost no selenium and satisfies the aforementioned emissions standard.

[0013] According to the wastewater treatment method described above, even hexavalent selenium that was impossible to remove conventionally can be sufficiently removed from wastewater and the wastewater standard (0.1 mg/liter) described above can be satisfied. Furthermore, because hexavalent selenium reduction can be performed simultaneously with denitrification treatment, the device configuration for the microbial treatment step can be achieved with the same device configuration (equipment configuration excluding activated sludge) as conventional wastewater treatment devices that perform a nitrification treatment (aerobic treatment) and a denitrification treatment (anaerobic treatment) without modification, and a wastewater treatment that includes selenium treatment is made possible readily and at a low cost with existing devices just by installing equipment for the step of removing tetravalent selenium, in this case. Furthermore, overall treatment time is markedly reduced compared to the case of performing hexavalent selenium reduction and denitrification treatment in different steps.

[0014] However, while the wastewater treatment method proposed by the applicants, as described above, is innovative in terms of providing an effective treatment method for wastewater that includes selenium for which there was no effective conventional method for removal, in order to improve functionality and further reduce costs of equipment or the like, the efficient reduction of hexavalent selenium is important, and there is a demand for the specific conditions to achieve this reduction efficiently be identified. Furthermore, in order to make the practicality of this technology more reliable and effective, the microorganisms with good ability to reduce hexavalent selenium must be specifically identified.

[0015] Here, the present invention is an improvement on

most of the selenium, excluding the small amount of tetravalent selenium dissolved in the wastewater, is removed from the wastewater by being captured in the sludge.

[0010] In addition, in the step of removing tetravalent selenium, an insolubilization treatment (tetravalent selenium insolubilization treatment) and a coagulation settling treatment (solid-liquid separation) are performed in order. The insolubilization treatment introduces wastewater after the microbial treatment step into the stirring tank and treats it by injecting a treatment agent (for example FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$) into the stirring tank to insolubilize the tetravalent selenium. According to this treatment, the tetravalent selenium (principal form: selenite SeO_3^{2-}) contained in the wastewater is insolubilized by reacting with the treatment agent as indicated in the following reaction formulas (1) and (2) or (3) and (4), for example, and becoming ferric selenite ($\text{Fe}_2(\text{SeO}_3)_3$).

[0011]

[Chem. 1]

treatment methods for wastewater containing nitrogen and selenium by the microbial treatment described above and has the main object of providing a wastewater treatment method that allows an efficient selenium removal treatment by setting treatment conditions, and has a further object of providing the wastewater treatment method using microorganisms identified for better efficiency.

[0016]

[Means for Solving the Problems] Whereas the inventors performed earnest research in order to achieve the objects described above, they obtained knowledge that the amount supplied of organic matter that is the nutrient source for the microorganisms is important and furthermore that the oxidation-reduction potential (ORP) settings are also important, and were led to the following invention based on this knowledge. Furthermore, the inventors discovered and deposited a selenate reducing bacteria that have effective reduction capability for hexavalent selenium.

[0017] That is to say, the wastewater treatment method according to claim 1 is a wastewater treatment method that removes at least nitrogen and hexavalent selenium from wastewater containing nitrogen and selenium by way of a microbial treatment that uses an activated sludge containing at least microorganisms having the ability to denitrify and microorganisms having the ability to reduce selenium, which reduce hexavalent selenium to tetravalent selenium and/or elementary selenium, characterized in that organic matter that is the nutrient source for the microorganisms in the activated sludge is added to a treatment tank in which the microbial treatment is implemented in an range exceeding the denitrification equivalent by 5 mg/liter-h or more.

[0018] Furthermore, the wastewater treatment method according to claim 2 is the wastewater treatment method according to claim 1 characterized in that selenate reducing bacterium FERM BP-5661 belonging to the genus *Pseudomonas* is used as the microorganism having the ability to reduce selenium.

[0019] Furthermore, the wastewater treatment method according to claim 3 is

characterized in that the oxidation-reduction potential in the treatment tank in which the microbial treatment is implemented is maintained to be no more than 300 mV.

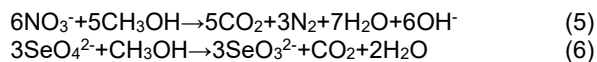
[0020] Furthermore, the wastewater treatment method according to claim 4 is characterized in that the oxidation-reduction potential in the treatment tank in which the microbial treatment is implemented is maintained to be the range no less than -200 mV and no more than 200 mV.

[0021] Furthermore, the wastewater treatment method according to claim 5 is characterized in that the concentration of nitrogen flowing into the treatment tank in which the microbial treatment is implemented is detected, and the dose of organic matter is adjusted on the basis of the detected value, so as to be within said range.

[0022]

[Modes of Embodiment of the Invention] Hereafter, one example of a mode of embodiment of the present invention is described based on the drawings. In FIG. 1, wastewater from a desulfurization device (not shown in the drawing) flows out as wastewater A1, via a normal coagulation settling step and COD treatment step as described in FIG. 6. The wastewater A1 contains a nitrogen component of NH_4^+-N , NO_2^--N , and NO_3^--N , and selenium dissolved from flue gas, for example approximately 0.3 mg/liter of hexavalent selenium. In addition, in this example, the wastewater A1 is first introduced into a nitrification tank 11 kept in aerobic conditions and undergoes an aerobic treatment (aerobic microbial treatment), then is introduced into a denitrification tank 12 kept in anaerobic conditions and undergoes an anaerobic treatment (anaerobic microbial treatment), further undergoes post-treatment in post-treatment equipment 13, and is discharged as treated wastewater B.

[0023] The aerobic treatment in the nitrification tank 11 uses activated sludge containing ammonia-oxidizing bacteria (bacteria having the property of producing NO_2^--N by oxidizing NH_4^+-N) and nitrite-oxidizing bacteria (bacteria having the property of producing NO_3^--N by oxidizing NO_2^--N), introduces and mixes the wastewater A1 into the nitrification tank 11 in which the activated sludge is floating or suspended, and aerates it



[0027] Note that N_2 generated by the above reaction is discharged into the atmosphere as a gas. Furthermore, some of the tetravalent selenium precipitates because the solubility is low compared to hexavalent selenium. Thus, a large amount of selenium, excluding the small amount of tetravalent selenium dissolved in the wastewater, is removed from the wastewater by being captured in the sludge.

[0028] In this anaerobic treatment, the methanol that is the nutrient source for the microorganisms is added to exceed the denitrification equivalent by 5 mg/liter-h or more. Furthermore, the methanol dose should be preferably maintained in a range exceeding the denitrification equivalent by 5-30 mg/liter-h. When these conditions are maintained, the reduction reaction for hexavalent selenium proceeds efficiently, and this is extremely advantageous in satisfying the wastewater standard value (0.1 mg/liter) with a large margin. Furthermore, by restricting the dose to a range exceeding the denitrification equivalent by 30 mg/liter, the COD value (chemical oxygen demand) increase and BOD bacteria proliferation in the wastewater is controlled, having the effect of making post-treatment easier.

[0029] That is to say, according to earnest research undertaken by the inventors, the activity of the denitrifying bacteria is strong and the denitrification reaction shown in formula (5) is prioritized in the denitrification tank 12; the

(exposes it to air) by blowing air. During this aerobic treatment in the nitrification tank 11, the NH_4^+-N in the wastewater becomes NO_2^--N by being oxidized by the ammonia-oxidizing bacteria in the activated sludge, and then the NO_2^--N becomes NO_3^--N by being oxidized by the nitrite-oxidizing bacteria in the activated sludge.

[0024] Next, the anaerobic treatment uses activated sludge containing microorganisms having the ability to reduce selenium, which reduce hexavalent selenium to tetravalent selenium and/or elementary selenium (for example the selenate reducing bacterium FERM BP-5661 described below), and denitrifying bacteria (bacteria having the property of producing N_2 by reducing NO_3^-), introduces and mixes wastewater A2 flowing out from the nitrification tank 11 into the denitrification tank 12 in which the activated sludge is floating or suspended, and maintains an anaerobic environment while supplying water-soluble organic matter such as methanol as a microorganism nutrient source. Note that one or a combination of two or more selected from an organic acid (for example, acetic acid), an alcohol (for example, methanol), an aldehyde, a ketone, a sugar (for example, glucose), an organic acid salt (for example, sodium acetate), and the like may be used as the nutrient source.

[0025] In the anaerobic treatment in the denitrification tank 12, after a suitable residence time, NO_3^- in the wastewater becomes N_2 as a result of being reduced by the denitrifying bacteria in the activated sludge, and the hexavalent selenium (principal form: selenate SeO_4^{2-}) in the wastewater is simultaneously reduced to tetravalent selenium (SeO_3^{2-}) by microorganisms having the ability to reduce selenium or further becomes elementary selenium. In this case (when methanol is used as the nutrient source), primarily the reactions in formulas (5) and (6) below occur in the denitrification tank 12.

[0026]

[Chem. 2]

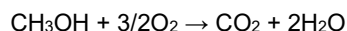
performance of the selenium reduction reaction shown in formula (6) was determined to be affected by the amount of organic matter remaining in the denitrification reaction; and the supplied amount of the organic matter that is the nutrient source of the microorganisms (methanol, for example) and the control of same is important in order to have the selenium reduction reaction performed efficiently along with the denitrification reaction during the anaerobic treatment. In addition, the inventors, by way of experiments and the like such as those described hereafter, researched preferable doses of organic matter, and identified the range for adding to exceed the denitrification equivalent by 5 mg/liter-h or more. Furthermore, it is established that when the dose of organic matter is increased without limit, the COD value (chemical oxygen demand) in the wastewater becomes high and a large amount of BOD bacteria proliferate, causing the post-treatment to be troublesome, and a range exceeding the denitrification equivalent by 30 mg/liter-h was found as an upper limit.

[0030] Note that adjustment of the dose of methanol described above is preferably performed automatically by way of a control device, specifically such as shown in FIG. 3, for example, on the basis of a detected value for the concentration of nitrogen flowing into the denitrification tank 12.

This control device comprises: a total nitrogen concentration meter 18 that detects the concentration of nitrogen flowing into the denitrification tank 12; a converter 19 that converts the detected value for the nitrogen concentration by this total nitrogen concentration meter 18 to a value corresponding to the preferable dose of methanol; and a flow rate adjusting valve 20 that adjusts the supply flow rate from a methanol reservoir 14 to a predetermined value by controlling the degree of opening in accordance with an output signal from this converter 19.

[0031] Here, the total nitrogen concentration meter 18 detects the total nitrogen concentration (NO_2^--N , NO_3^--N) flowing into the denitrification tank 12 using ion chromatography or absorptiometry, for example. Note that the location for detecting the total nitrogen concentration is not limited to the wastewater inlet to the denitrification tank 12, but may also be the wastewater inlet to the nitrification tank 11 as shown in FIG. 3. However, when using the wastewater inlet to the nitrification tank 11, NH_4^+-N , NO_2^--N , and NO_3^--N must be detected as the total nitrogen concentration.

[0032] Furthermore, by calculating $T = \text{total nitrogen concentration (mg/liter-h)} \times 1.9 + \text{excess dose } \alpha \text{ (mg/liter-h)}$, the converter 19 generates and outputs a signal corresponding to the calculated dose of methanol T, in which the aforementioned excess dose α ($\alpha = 5$ to 30) is added to the theoretical denitrification equivalent. Note that, here, the numerical value of 1.9 is found from the relationship of the molecular weights in the reaction formula (5), that is to say from the calculation of $(5 \times \text{CH}_3\text{OH})/(6 \times \text{N})$



[0037] Thus, problems such as an increased COD value due to excess methanol are reliably prevented. Then, the wastewater A4 guided from the aeration tank 21 is introduced to a settling tank 22 and sedimentation separation is performed here, and the high-concentration sludge C is returned the nitrification tank 11 and circulated. Note that the sludge C returned in this manner contains the partially precipitated tetravalent selenium, but the accumulation thereof is prevented by removal by suitably discharging this along with bacteria that have proliferated excessively.

[0038] In addition, with the wastewater A5 that is guided from the settling tank 22, the tetravalent selenium in the liquid is removed in a step of removing tetravalent selenium with tetravalent selenium removal equipment 23, and this is discharged as treated wastewater B. Note that in the step of removing tetravalent selenium, an insolubilization treatment (tetravalent selenium insolubilization treatment) and a coagulation settling treatment (solid-liquid separation) are performed in that order, in the same manner as in the wastewater treatment method shown in FIG. 6 described above.

[0039] The insolubilization treatment introduces the wastewater A5 into the stirring tank, and inputs a treatment agent (for example FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$) into the stirring tank to insolubilize the tetravalent selenium, and mixes same into the wastewater. With this treatment, the tetravalent selenium (principal form: selenite SeO_3^{2-}) contained in the wastewater is insolubilized by forming ferric selenite ($\text{Fe}_2(\text{SeO}_3)_3$) by bringing about the reaction with the treatment agent as indicated in the reaction formulas (1) and (2), or (3) and (4) described above.

[0040] Thus, in the next coagulation sedimentation treatment, when the wastewater is separated into solid and liquid by a coagulation settling device or the like, the tetravalent selenium is separated to the solid-phase side as ferric selenite, insolubilized and incorporated into the discharged solids (sludge). Accordingly, the treated wastewater B contains virtually no selenium and satisfies the aforementioned emissions standard with a large margin. Note that the sludge

$$\text{O}_3-\text{N}) = (5 \times 32)/(6 \times 14).$$

[0033] Furthermore, during the anaerobic treatment, the oxidation-reduction potential (ORP) is controlled to be no more than 300 mV and preferably -200 mV to 200 mV. Thus, as demonstrated in the experimental results described below, the hexavalent selenium reduction performance is further increased. Furthermore, operations are usually performed with the DO value (dissolved oxygen amount) in the anaerobic treatment at 0.1 - 0.01 mg/liter, for anaerobic conditions, to keep microbial activity high. Furthermore, this is usually run with pH at approximately 7.5 from the viewpoint of microbial activity.

[0034] Note that control of the oxidation-reduction potential and DO value or pH is performed by manipulating the methanol dose, and the stirring and the air volume for aeration in the upstream nitrification tank 11 on the basis of a pH meter 15, ORP meter 16, or DO meter 17 provided in the denitrification tank 12.

[0035] Next, post-treatment in the post-treatment equipment 13 is executed with the equipment and procedures shown in FIG. 2, for example. That is to say, wastewater A3 flowing from the denitrification tank 12 is introduced into an aeration tank 21, and remaining methanol is decomposed here by the following reaction (7) by way of blowing in air.

[0036]

[Chem. 3]

(7)

removed in the coagulation settling treatment may be treated as industrial waste as is, but handling of same is easy by, for example, discarding as a dewatered cake produced by a centrifugal sedimentation machine or the like. Note that most of the selenium in this sludge is present in an insolubilized form, so the leaching standard is sufficiently satisfied even if this is discarded as a cake or the like.

[0041] With the wastewater treatment method described above, as demonstrated in an embodiment described hereafter, even hexavalent selenium that was impossible to remove conventionally can be sufficiently removed from wastewater efficiently, and the wastewater standard (0.1 mg/liter) described above can be satisfied with a large margin. Note that the step of removing tetravalent selenium is not necessarily required, because the concentration of selenium (primarily tetravalent selenium) remaining in the wastewater after the microbial treatment step is no more than the emissions standard value as a result of selenium removal activity during the microbial treatment step, depending on a management of the concentration of selenium in the wastewater or the capacity and metabolic state of the microbial treatment. Furthermore, the example of adding a treatment agent for insolubilizing tetravalent selenium to the wastewater after separating the sludge, following the microbial treatment step, was described here, but the insolubilized selenium may be separated with the sludge in a later solid-liquid separation step by adding the treatment agent to the wastewater after the microbial treatment step, before separating the sludge.

[0042]

[Embodiments] Note that the inventors performed the experiments described below as one embodiment in order to demonstrate the aforementioned effects, and these are described below. Note that the following experiments use an activated sludge that is acclimated for approximately 14 days in a sealed anaerobic environment in which the concentration of hexavalent selenium is approximately 10 ppm, and which contains denitrifying bacteria used in a denitrification treatment in a wastewater treatment device in an existing flue gas desulfurization system. Note that, in terms of microorganisms to reduce hexavalent selenium in the activated sludge, at least one strain belonging to the genus *Pseudomonas* was identified as a new bacterium discovered by the inventors as described below and was deposited as FERM BP-5661.

[0043] Experiment 1. First, experiment 1 analyzed the relationship between the hexavalent selenium reduction performance and the excess amount of methanol, with respect to the denitrification equivalent, added, using a test device (flow-through type test device)

with the same configuration as the device shown in FIG. 1 and FIG. 2, and changing the methanol dose to the denitrification tank under the conditions shown in Table 1. The results are shown in FIG. 4. Here, the excess methanol dose (mg/liter·h) indicates the amount of methanol (mg) per unit time (h), unit volume (liter). Furthermore, the methanol dose is determined by a calculation based on the NO_3^- -N concentration in the liquid at the denitrification tank inlet. The test results confirmed that performance of hexavalent selenium reduction was improved by adding methanol added as the nutrient source for microorganisms so as to exceed the denitrification equivalent by 5 mg/liter·h or more.

[0044]

[Table 1]

Table 1 Test conditions for reduction of hexavalent selenium by microorganisms

Item	Condition
Wastewater flow rate	1 liter/h
Wastewater composition	
* Hexavalent selenium concentration	0.32 mg/liter
* Tetraivalent selenium concentration	0.03 mg/liter
* NH_4^+ -N concentration	56 mg/liter
* NO_2^- -N concentration	< 1 mg/liter
* NO_3^- -N concentration	24 mg/liter
Concentration of floating matter in activated sludge	
* Nitrification tank	2080 mg/liter
* Denitrification tank	2050 mg/liter
Temperature	25°C
pH (nitrification tank, denitrification tank)	7.5
Stirring	Yes
Liquid volume in each tank	
* Nitrification tank	7 liters
* Denitrification tank	12 liters
* Post-treatment tank	3 liters
Nutrition source	Methanol
ORP (denitrification tank)	-50 mV
DO (denitrification tank)	0.05 mg/liter

[0045] Note that results of evaluating denitrification performance at the same time were that NH_4^+ -N, NO_2^- -N, and NO_3^- -N were 1 mg/liter or less at the denitrification tank outlet, whereas NH_4^+ -N and NO_2^- -N was 1 mg/liter or less and NO_3^- -N was 78 mg/liter at the denitrification tank inlet, sufficiently demonstrating denitrification performance. Furthermore, FeCl_3 was added, so as to be 100 mg/liter, to the wastewater at the outlet of the denitrification tank that was tested under the conditions of adding methanol so as to exceed the denitrification equivalent by 5 mg/liter·h or more, and the results of implementing the tetraivalent selenium insolubilization treatment were that the total selenium concentration in the liquid sufficiently satisfied the emissions standard (0.1 mg/l) with a large margin.

[0046] Experiment 2. Next, experiment 2 analyzed the impact of oxidation-reduction potential on the performance of hexavalent selenium reduction, using a test device (flow-through type test device) with the same configuration as the device shown in FIG. 1 and FIG. 2 and changing the oxidation-reduction potential (ORP), with the conditions other than ORP set to the

conditions shown in Table 1. The results are shown in FIG. 5. As shown in FIG. 5, improvement in the performance of hexavalent selenium reduction by adjusting the oxidation-reduction potential in the denitrification tank to 300 mV or less, preferably to -200 mV to 200 mV, was confirmed.

[0047] Experiment 3. Next, experiment 3 implemented a test to evaluate the performance of hexavalent selenium reduction under the conditions in Table 1, using a test device (flow-through type test device) with the same configuration as the device (one comprising a methanol dose control device) shown in FIG. 2 and FIG. 3. Note that, in this experiment, the total nitrogen concentration (NH_4^+ -N, NO_2^- -N, and NO_3^- -N) in the wastewater inlet of the nitrification tank was detected. Furthermore, a spectrometer using ion chromatography was used as the total nitrogen concentration meter 18.

The test results are shown in Table 2. As shown in Table 2, improvement in the performance of hexavalent selenium reduction by detecting the total nitrogen concentration flowing into the denitrification tank and performing control on the basis of this, so as to add a dose of methanol exceeding the denitrification equivalent by 5 mg/liter-h or more,

was confirmed.

[0048]

[Table 2]

Table 2 Test results for reduction of hexavalent selenium by microorganisms

Results of analysis of liquid input into the denitrification tank (mg/liter)			Results of analysis of liquid discharged from the denitrification tank (mg/liter)			Excess methanol for equivalent denitrification (mg/liter-h)
All nitrogen	Hexavalent selenium	Tetravalent selenium	All nitrogen	Hexavalent selenium	Tetravalent selenium	
4.2	0.32	0.03	<0.1	0.24	0.10	2.1
4.1	0.31	0.02	<0.1	0.05	0.25	5.0
4.2	0.33	0.04	<0.1	0.02	0.28	12.3
4.3	0.30	0.02	<0.1	0.01	0.27	15.4
8.0	0.31	0.04	<0.1	0.25	0.09	2.3
8.1	0.30	0.03	<0.1	0.06	0.24	5.1
7.9	0.29	0.01	<0.1	0.02	0.25	11.0
8.3	0.33	0.02	<0.1	0.01	0.28	15.6
8.2	0.31	0.03	<0.1	0.01	0.27	30.4

[0049] Note that an example of a method of culturing and isolating selenate reducing bacterium FERM BP-5661 is described next. In order to investigate a microorganism for effectively reducing selenate, the inventors isolated a microorganism from activated sludge that was used in a denitrification treatment in a conventional wastewater treatment device using the following method, and as a result of examining selenate reduction performance a new strain of the genus *Pseudomonas* that effectively reduced selenate was discovered. Then this was named *Pseudomonas* sp. SR-34, and as a result of depositing this at the National Institute of Bioscience and Human Technology, at the Agency of Industrial Science and Technology was that this was accepted as FERM BP-5661.

[0050] Culturing to separate the selenate reducing bacterium FERM BP-5661 (hereafter, the present strain) used in this example was performed using the PYG selenate medium shown in Table 3. First, 3 milliliters of PYG selenate medium was poured into a 7-milliliter capacity test tube with a screw cap, 3% by volume of a sample of activated sludge used in the denitrification treatment described above was added, and this was cultured at 27°C under static conditions. Note that "Selenate" in Table 3 is hexavalent selenium, specifically Na_2SeO_4 .

[0051]

[Table 3]

Table 3 PYG selenate medium composition

Peptone	2.0 g/l
Yeast Extract	1.0 g/l
Glucose	0.5 g/l
Selenate	20 mM
pH	7.2

[0052] Note that in order to examine the characteristics of the present strain, the PYA selenate medium shown in Table 4, in which the glucose in the PYG selenate medium was replaced with sodium acetate,

and the selenate inorganic salt medium shown in Table 5, in which 20 mM of selenic acid was added to an inorganic salt medium with acetic acid as a single carbon source, were also used in some cases.

[0053]

[Table 4]

Table 4 PYA selenate medium composition

Peptone	2.0 g/l
Yeast Extract	1.0 g/l
Sodium Acetate	0.5 g/l
Selenate	20 mM
pH	7.2

[0054]

[Table 5]

Table 5 Inorganic salt selenate medium (in 1000 ml)

Na ₂ HPO ₄ + KH ₂ PO ₄ buffer solution (1M: pH 6.8)	40 ml
(NH ₄) ₂ SO ₄	1.0 g
Hutner inorganic salt solution	20 ml
Sodium Acetate	20 mM
Selenate	20 mM

[0055] Note that the composition of the Hutner inorganic salt solution in Table 5 is shown in Table 6, and the composition of Metals "44" in Table 6 is shown in Table 7. Here, "Nitrilotriacetic Acid" in Table 6 means nitrilotriacetic acid, and "EDTA" in Table 7 is ethylenediaminetetraacetic acid. Furthermore, the Hutner

inorganic salt solution is created by dissolving nitrilotriacetic acid in distilled water, neutralizing with approximately 7.3 g of potassium hydroxide, and then adding the remaining salts. Furthermore, a few drops of sulfuric acid is added to Metals "44" so as to prevent the formation of sediment.

[0056]

[Table 6]

Table 6 Hutner inorganic salt solution (in 1000 ml)

Nitrilotriacetic Acid	10 g
MgSO ₄ ·7H ₂ O	14.45 g
CaCl ₂ ·2H ₂ O	3.335 g
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	9.25 mg
FeSO ₄ ·7H ₂ O	99 mg
Metals"44"	50 ml

[0057]

[Table 7]

Table 7 Metals "44" (in 1000 ml)

EDTA	250 mg
ZnSO ₄ ·7H ₂ O	1095 mg
FeSO ₄ ·7H ₂ O	500 mg
MnSO ₄ ·H ₂ O	154 mg
CuSO ₄ ·5H ₂ O	39.2 mg
Co(NO ₃) ₂ ·6H ₂ O	24.8 mg
Na ₂ B ₄ O ₇ ·10H ₂ O	17.7 mg

[0058] In addition, separation of the present strain was performed as follows. That is to say, a culture solution (that is to say, one having the ability to reduce selenate) that generated a red sediment due to the formation of elementary selenium in the culturing treatment described above was anaerobically cultured at 27°C by dilution plating in a PYG selenate plating medium for 7 days. Then, a colony showing red in the plating medium was selected as selenate reducing bacteria, and single colony isolation was repeated with the same medium and culture conditions to purify the selenate reducing bacteria. Note that single colony isolation means selection of a specific bacterial strain by way of cultivating only a specific colony generated on the medium on a separate, new medium.

[0059] Next, the microbiological characteristics of the present strain are described. The biochemical characterization of the present strain was carried out according to "Classification and identification of microorganisms (Part 2)" (written and edited by Takeharu Hasegawa, published by Gakukai Shupan Center). Furthermore, simple identification tests using ID Test NF-18 (Nissui Pharmaceutical), and BBL Crystal E/NF (Becton, Dickinson), which are simple commercial identification kits, were also performed. First, the microbiological characteristics of the present strain are shown in Table 8.

[0060]

[Table 8]

Table 8 Basic properties of selenate reducing bacteria

Shape	bacillus
Size	0.4 × 1.0 μm
Gram stain	-
Mobility	+
Flagella	Polar flagella
Aerobic proliferation	+
Anaerobic proliferation	+
Catalase	+
Oxidase	+
OF test	O
Pigment generation	-
Fluorescent pigment generation	-
Proliferation at 42°C	-
Tween 80 hydrolysis	+
Starch hydrolysis	-
PHB accumulation	-

[0061] The present strain is a gram-negative bacillus and has mobility due to polar flagella. Furthermore, it is a facultative anaerobic bacterium, for which oxidase tests and catalase tests are positive, and aerobically produces acid from glucose (OF test = O). Furthermore, it forms colonies that spread thinly over a large area on the plating medium. From these basic characteristics, the present strain was recognized as a strain belonging to genus *Pseudomonas*. Note that the present strain is cultivated in an inorganic salt medium with acetic acid as a single carbon source, and is not thought to be auxotrophic.

[0062] Next, the results of the Nissui Pharmaceutical ID test NF-18 are summarized in Table 9. These results were compared against the database included, but there were no bacterial strains corresponding to the present strain.

[0063]

[Table 9]

Table 9 Results of the Nissui ID test-NF-18

Acid production from glucose	+
Acid production from fructose	+
Acid production from maltose	-
Acid production from galactose	-
Acid production from xylose	+
Acid production from mannitol	+
Acid production from sucrose	-
Acid production from lactose	-
Hydrolysis of esculin	-
Hydrolysis of urea	-
Utility of citric acid	+
β-galactosidase	-
Lysine decarboxylase	-
Arginine dihydrolase	-
Ornithine decarboxylase	-
Indole production	-
Gelatin liquefaction	-

[0064] Next, the results of BBL Crystal E/NF are shown in Table 10 and Table 11. When the results were compared against a database, the present strain was determined with 83% certainty to be a bacterium belong to *Pseudomonas aeruginosa*. Note that there are no well-known reports of a strain having the ability to reduce selenium in the bacteria belonging to *Pseudomonas aeruginosa*. Accordingly, the present strain was thought to be a new strain.

[0065]

[Table 10]

Table 10 Results of BBL CRYSTAL E/NF (part 1)

Acid production from arabinose	-
Acid production from mannose	-
Acid production from sucrose	-
Acid production from melibiose	-
Acid production from rhamnose	-
Acid production from sorbitol	-
Acid production from mannitol	-
Acid production from adonitol	-
Acid production from galactose	-
Acid production from inositol	-
p-nitrophenyl phosphate	+
p-nitrophenyl α - β -glucoside	-
p-nitrophenyl galactoside	-
Proline nitroanilide	+

[0066]

[Table 11]

Table 11 Results of BBL CRYSTAL E/NF (part 2)

p-nitrophenyl bisphosphate	-
p-nitrophenyl xyloside	-
p-nitrophenyl α -arabinoside	-
p-nitrophenyl phosphorylcholine	-
p-nitrophenyl β -glucuronide	-
p-nitrophenyl N-acetyl-glucosaminide	-
L- γ -glutamyl p-nitroanilide	+
Hydrolysis of esculin	-
Phenylalanine production	+
Hydrolysis of urea	+
Glycine decomposition	+
Utility of citric acid	+
Utility of malonic acid	+
Reduction of tetrazolium	-
Arginine dihydrolase	+
Lysine decarboxylase	-

[0067] Next, a test for selenate reduction by pure, isolated present strain is described. As described above, it is known that a colony shows red, and selenate is reduced to elementary selenium when the present strain is cultured on a PYG selenate plating medium. Note that colonies in PYG plating mediums to which selenate was not added did not turn red.

[0068] Furthermore, a reduction test in a methanol medium containing hexavalent selenium, as shown in Table 12, was performed. The present strain was added to 1 liter of this methanol medium so as to reach 250 mg/liter and, after stirring and mixing in a flask and sealing in an anaerobic environment, was kept and cultured for 24 hours while stirring at 25°C. In addition, the results of analyzing the hexavalent selenium in the supernatant liquid were that none was detected after 24 hours although there was 10 mg/liter initially. Furthermore, the sediment generated as a result of culturing showed red, and the results of energy dispersive X-ray spectroscopy analysis confirmed that this was elementary selenium. Therefore, most of the hexavalent selenium is known to have been reduced to elementary selenium.

[0069]

[Table 12]

Table 12 Composition of methanol medium

Na ₂ SeO ₄	24 mg
CH ₃ OH	500 mg
KNO ₃	1.0 g
Na ₂ SO ₄	1.0 g
KH ₂ PO ₄	0.5 g
MgSO ₄ ·7H ₂ O	0.1 g
Distilled water	1.0 liters

[0070] Note that the present strain can be cultured in mediums other than the medium described above, as the specificity with respect to nutrient sources is low. For example, the inventors confirmed that culturing was possible even with heart infusion broth (manufactured by Nissui Pharmaceutical). Furthermore, the present strain can be cultured even in aerobic conditions.

[0071] Furthermore, the present invention is not limited to the aspect described above but may have various aspects. For example, the residual methanol decomposition treatment in the aeration tank 21 in the post-treatment shown in FIG. 2 is not necessarily required if the amount of residual methanol is a small at the outlet of the denitrification tank 12, due to the concentration of selenium in the source wastewater or the like. Furthermore, as described above, the step of removing tetravalent selenium is not necessarily required when the concentration of selenium (primarily tetravalent selenium) remaining in the wastewater after the microbial treatment is no more than a desired value, as a result of the selenium removing action in microbial treatment. Furthermore, the wastewater treatment method of the present invention can be applied not only to desulfurization wastewater but to any wastewater if the wastewater contains nitrogen compounds and hexavalent selenium.

[0072]

[Effects of the Invention] With the wastewater treatment method of the present invention, hexavalent selenium in wastewater can be readily removed as solids, because this is reduced to tetravalent selenium and/or elementary selenium during a microbial treatment. That is to say, much of the selenium can be removed as solids in this treatment because the solubility of elementary selenium is low and tetravalent selenium can be readily insolubilized, for example, as ferric selenite having a very low solubility.

For this reason, even when hexavalent selenium that could not be conventionally removed from wastewater is present, the concentration thereof can be markedly reduced and the emissions standard for selenium can be satisfied.

[0073] In particular, with the present invention, organic matter that is the nutrient source for microorganisms is added to a treatment tank in which the microbial treatment is implemented, so as to be in a range exceeding the denitrification equivalent by 5 mg/liter·h or more. Thus, because the performance of reducing hexavalent selenium by the microbial treatment is markedly improved, a large margin with respect to the emissions standard can be maintained due to improvement in treatment performance and a more compact and lower cost treatment tank and other wastewater treatment equipment can be achieved.

[0074] Furthermore, the configuration of wastewater treatment equipment is simplified because both selenium reduction and denitrification treatment are performed during the microbial treatment, using activated sludge that contains at least a microorganism having the ability to denitrify and a microorganism having the ability to reduce selenium that reduces hexavalent selenium to tetravalent selenium and/or elementary selenium. That is to say, if the selenium removal treatment is performed in a separate step by using an activated sludge that is different than the denitrification treatment, for example, a device dedicated to the selenium removal treatment (for example a stirring tank for the microbial treatment) must be provided separately, but the same device can be shared in the configuration of this invention.

[0075] In other words, with existing wastewater treatment devices that perform denitrification treatment with conventional microbial treatment, the treatment method of the present invention can be implemented as-is, and a highly efficient removal treatment for hexavalent selenium is possible simply by changing the activated sludge being used, without modifying the device configuration. Furthermore, with this configuration, the treatment time required for the overall wastewater treatment can be reduced because the selenium reduction is performed simultaneously with the denitrification treatment.

[0076] Furthermore, as described in claim 3, when the oxidation-reduction potential in the treatment tank in which the microbial treatment is implemented is kept to 300 m

V or less, the performance of hexavalent selenium reduction due to the microbial treatment is further improved and further improvement of treatment performance, equipment downsizing, and the like can be achieved.

[0077] Furthermore, in particular, as described in claim 4, when the oxidation-reduction potential in the treatment tank in which the microbial treatment is implemented is kept in the range of -200 mV or more to 200 mV or less, the performance of hexavalent selenium reduction due to the microbial treatment is significantly improved and effect of treatment performance improvement, equipment downsizing, and the like is particularly significant.

[Brief Description of the Drawings]

[FIG. 1] This is a drawing showing wastewater treatment facility in which a wastewater treatment method of the present invention is applied.

[FIG. 2] This is a drawing showing post-treatment equipment in a wastewater treatment facility in which a wastewater treatment method of the present invention is applied.

[FIG. 3] This is a drawing showing another example of a wastewater treatment facility (one comprising a methanol dose control device) in which a wastewater treatment method of the present invention is applied.

[FIG. 4] This is a drawing showing the results of experiment 1 (test to evaluate the impact of methanol dose) to demonstrate the effect of the present invention.

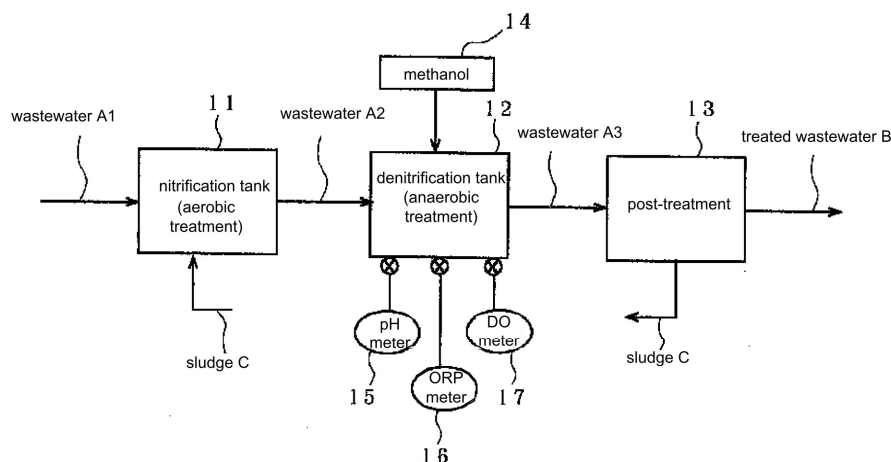
[FIG. 5] This is a drawing showing the results of experiment 2 (test to evaluate the impact of oxidation-reduction potential) to demonstrate the effect of the present invention.

[FIG. 6] This is a drawing showing a wastewater treatment method (earlier proposed by the applicant) on which the present invention is based.

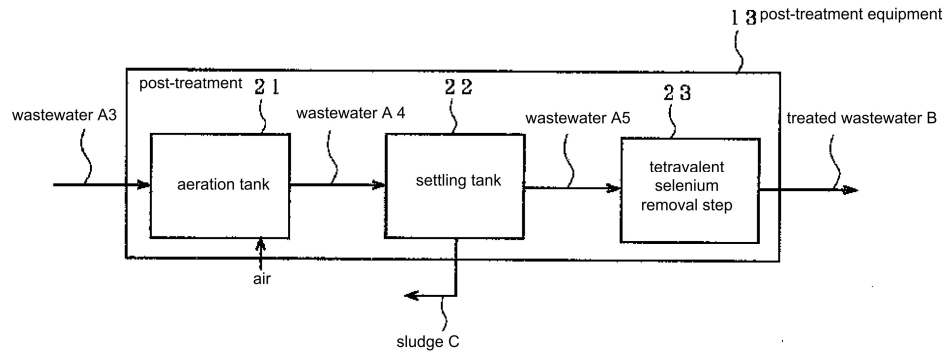
[Explanation of the Symbols]

- 12 denitrification tank (treatment tank)
- 14 methanol reservoir
- 16 ORP meter (oxidation-reduce potentiometer)
- 18 total nitrogen concentration meter
- 19 converter
- 20 flow rate adjusting valve

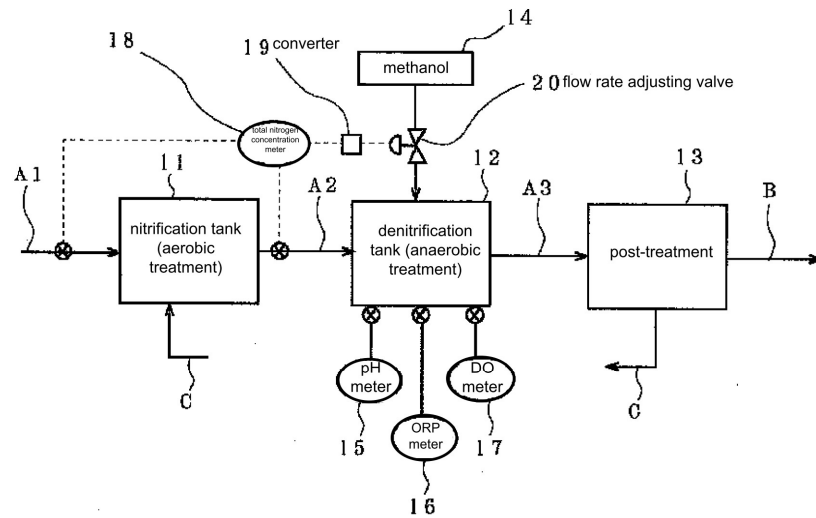
[FIG. 1]



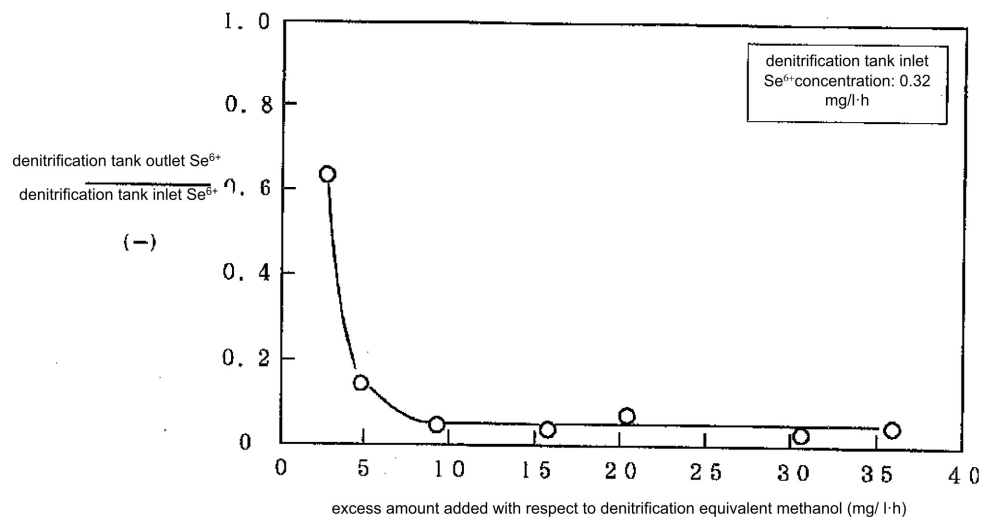
[FIG. 2]



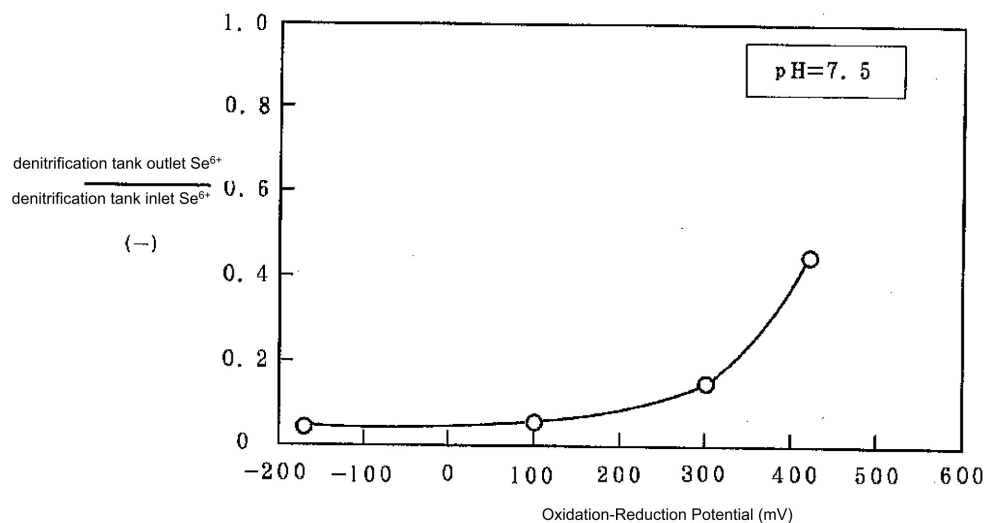
[FIG. 3]



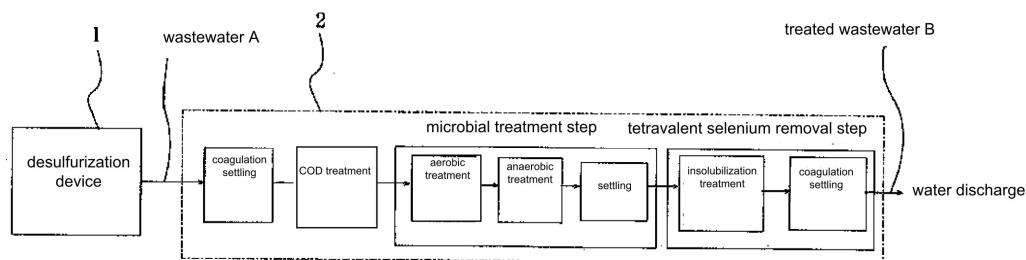
[FIG. 4]



[FIG. 5]



[FIG. 6]



Continued from the front page

(72) **Inventor:** NAGAYASU, Tatsuto
Mitsubishi Heavy Industries, Ltd.
2-5-1 Marunouchi, Chiyoda-ku, Tokyo-to

(72) **Inventor:** KANEKO, Masahito
Mitsubishi Heavy Industries, Ltd.
Hiroshima laboratory
4-6-22 Kanonshinmachi, Nishi-ku,
Hiroshima-shi, Hiroshima-ken

(72) **Inventor:** OGUSHI, Yasuyuki
Mitsubishi Heavy Industries, Ltd.
Hiroshima laboratory
4-6-22 Kanonshinmachi, Nishi-ku,
Hiroshima-shi, Hiroshima-ken

(72) **Inventor:** OKINO, Susumu
Mitsubishi Heavy Industries, Ltd.
Hiroshima laboratory
4-6-22 Kanonshinmachi, Nishi-ku,
Hiroshima-shi, Hiroshima-ken

(72) **Inventor:** HINO, Masao
Mitsubishi Heavy Industries, Ltd.
Hiroshima laboratory
4-6-22 Kanonshinmachi, Nishi-ku,
Hiroshima-shi, Hiroshima-ken

(72) **Inventor:** TAKAKURA, Mitsuaki
Electric Power Development Co.,Ltd.
6-15-1 Ginza, Chuou-ku, Tokyo-to

(72) **Inventor:** MUTO, Kenichi
Electric Power Development Co.,Ltd.
6-15-1 Ginza, Chuou-ku, Tokyo-to

(72) **Inventor:** TAKAGI, Kenji
Electric Power Development Co.,Ltd.
6-15-1 Ginza, Chuou-ku, Tokyo-to

(72) **Inventor:** HARUNA, Yasutoshi
Electric Power Development Co.,Ltd.
6-15-1 Ginza, Chuou-ku, Tokyo-to

(72) **Inventor:** MIYAGATA, Teiji
Electric Power Development Co.,Ltd.
6-15-1 Ginza, Chuou-ku, Tokyo-to

Certification of Translation

Translator's Declaration: May 16, 2017

I, Carl McBee, hereby declare:

That I possess advanced knowledge of the Japanese and English languages. My qualifications are as follows:

- More than eighteen years as a Japanese technical translator
- Master of Science in Engineering (Technical Japanese Program) from University of Washington
- Formerly the Senior Bilingual Technical Writer at Nintendo of America
- US Department of Defense certification of General Professional Proficiency in Japanese

The attached translation is, to the best of my knowledge and belief, a true and accurate translation from Japanese to English of Japanese Unexamined Patent Application Number JP-10-249392-A. I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. 1001), and may jeopardize the validity of the application or any patent issuing thereon. I declare under penalty of perjury that all statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true.

Carl McBee

