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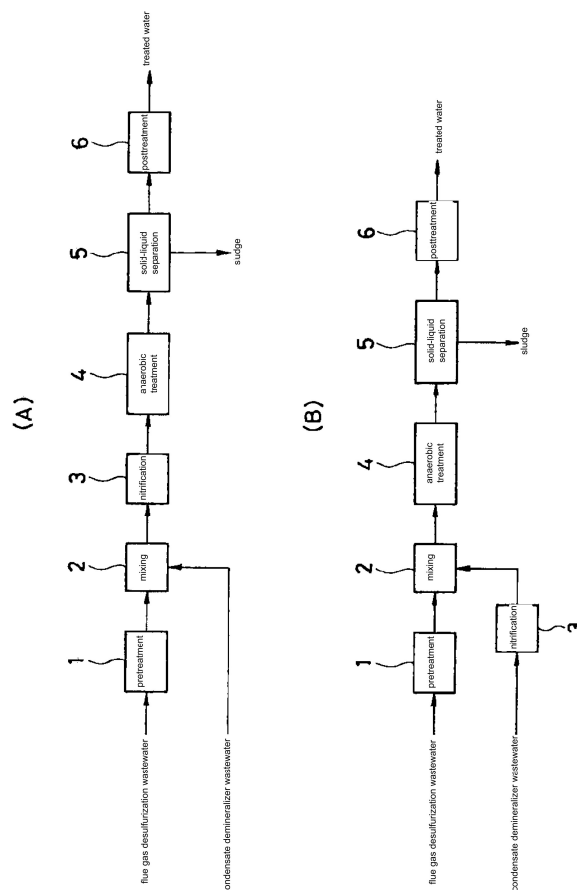
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(54) Title of the Invention: Method for treating flue gas desulfurization wastewater

(57) [Abstract]

[Problem] To propose a method for treating flue gas desulfurization wastewater, which can efficiently remove selenium in the flue gas desulfurization wastewater, and can efficiently remove ammoniacal nitrogen from condensate demineralizer wastewater.

[Means for Solving the Problem] A method of treating flue gas desulfurization wastewater wherein: in a pretreatment step 1, the bioinhibitory substances are removed from flue gas desulfurization wastewater containing selenium; in a nitrification step 3, ammoniacal nitrogen included in condensate demineralizer wastewater is contacted with biological sludge including sulfurizing [sic] bacteria, in an aerobic state, so as to be biologically nitrified before or after being mixed with the flue [sic] desulfurization wastewater; in a mixing step 2, pretreated flue gas desulfurization wastewater is mixed with condensate demineralizer wastewater, before nitrification or after nitrification; in an anaerobic treatment step 4, mixed wastewater, after mixing and nitrification, is contacted with biological sludge including denitrifying bacteria, in an anaerobic state, so as to perform denitrification and reduce selenium compounds; and in a solid-liquid separation step 5, sludge to which insolubilized selenium compounds have been adsorbed is subjected to solid-liquid separation.



[Claims]

[Claim 1] A method for treating flue gas desulfurization wastewater comprising: a pretreatment step of removing bioinhibitory substances from flue gas desulfurization wastewater containing selenium; a nitrification step of contacting ammoniacal nitrogen included in condensate demineralizer wastewater with biological sludge including nitrifying bacteria, in an aerobic state, so as to be biologically nitrified before or after being mixed with the flue gas desulfurization wastewater; a mixing step of mixing pretreated flue gas desulfurization wastewater with condensate demineralizer wastewater, before nitrification or after nitrification; an anaerobic treatment step of contacting mixed wastewater, after mixing and nitrification, with biological sludge including denitrifying bacteria, in an anaerobic state, so as to perform denitrification and reduce selenium compounds; and a solid-liquid separation step of subjecting sludge, to which selenium compounds that have been insolubilized by reduction have been adsorbed, to solid-liquid separation.

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

The present invention relates to a method for treating flue gas desulfurization wastewater containing selenium, by mixing with condensate demineralizer wastewater containing ammoniacal nitrogen.

[0002]

[Prior Art] When wet desulfurization is performed with a device for desulfurization of flue gas that is generated by combustion of fuel such as coal or petroleum in thermal power plants, selenium may be contained in the flue gas desulfurization wastewater discharged from the desulfurization device. Because such flue gas desulfurization wastewater contains COD components, in addition to selenium, adsorption treatment is performed with activated carbon or a resin for COD adsorption. Such an adsorption step is a process specific to this wastewater, and therefore flue gas desulfurization wastewater was treated separately from condensate demineralizer wastewater and dust precipitation wastewater, which are also generated in thermal power plants.

[0003] Here, a condensate demineralizer is an ion exchange device, with which demineralization is performed, in order to use the condensate generated by the condenser as boiler supply water, but if the ion exchange resin is of the ammonia-type, wastewater containing ammonium sulfate will be produced when this is regenerated with sulfuric acid. Conventionally, such wastewater containing ammoniacal nitrogen was neutralized and subjected to other chemical treatment, together with other wastewater generated in the demineralizer.

[0004] It is of note that there exists a biological treatment method in which selenium compounds are reduced by contacting selenium-containing water with biological sludge, in an anaerobic state, which serves as a treatment method for rendering wastewater containing selenium compounds such as those of Se^{6+} , Se^{4+} harmless. For example, in terms of biological reactions with selenium compounds, it has been reported that Se^{6+} and Se^{4+} are reduced in the presence of lactose by selenate (selenite) reducing bacteria, in *Proceedings of the Annual Conference of the Japan Society on Water Environment*, 1995, p. 176. This method employs a selenate (selenite) reducing bacterium, isolated from sites contaminated with selenium compounds, for the reduction of selenium compounds, and thus treatment is difficult because a special bacterium is used.

[0005]

[Problems to Be Solved by the Invention] An object of the present invention is to propose a method for treating flue gas desulfurization wastewater, which can efficiently remove

selenium in flue gas desulfurization wastewater by performing treatment with a combination of flue gas desulfurization wastewater and condensate demineralizer wastewater, and also can efficiently remove ammoniacal nitrogen in demineralizer wastewater.

[0006]

[Means for Solving the Problems] The present invention is a method of treating flue gas desulfurization wastewater comprising: a pretreatment step of removing bioinhibitory substances from flue gas desulfurization wastewater containing selenium; a nitrification step of contacting ammoniacal nitrogen included in condensate demineralizer wastewater with biological sludge including nitrifying bacteria, in an aerobic state, so as to be biologically nitrified before or after being mixed with the flue gas desulfurization wastewater; a mixing step of mixing pretreated flue gas desulfurization wastewater with condensate demineralizer wastewater, before nitrification or after nitrification; an anaerobic treatment step of contacting mixed wastewater, after mixing and nitrification, with biological sludge including denitrifying bacteria, in an anaerobic state, so as to perform denitrification and reduce selenium compounds; and a solid-liquid separation step of subjecting sludge, to which selenium compounds that have been insolubilized by reduction have been adsorbed, to solid-liquid separation.

[0007] In the present invention, "selenate (selenite)" means "selenate and/or selenite." In addition, " Se^{6+} ", " Se^{4+} ", " Se^0 " and " Se^{2-} " mean selenium with oxidation numbers of +VI, +IV, 0 or -II, respectively. These may also be referred to simply as Se. In the present invention, "nitrate (nitrite)" means nitrate and/or nitrite."

[0008] In the present invention, the flue gas desulfurization wastewater to be treated is wastewater discharged from a device for wet desulfurization of flue gas, which is generated by combustion of fuel such as coal or petroleum, the wastewater containing selenium compounds such as selenate (selenite), and usually containing sulfate ions, COD components and the like, in addition to selenium compounds.

[0009] In the present invention, the condensate demineralizer wastewater to be treated is wastewater containing regeneration effluent from regeneration of ion exchange resin in a demineralizer that demineralizes condensate produced by a condenser. Among the types of wastewater discharged from condensate demineralizers, ammoniacal nitrogen-containing wastewater that contains regeneration effluent resulting from desorbing ammonium ions from an ammonia-type cation exchange resin, and washing wastewater from the same, are suitable for the treatment of the present invention, but the wastewater may also result from mixing with other types of wastewater.

[0010] In the present invention, a pretreatment for removing bioinhibitory substances from the flue gas desulfurization wastewater is first performed in a pretreatment step. Flue gas desulfurization wastewater contains inhibitory substances such as heavy metal ions and fluoride ions, and therefore a pretreatment such as settling and/or coagulation settling is performed in order to remove these. Settling is the gravitational separation of solids that have already been precipitated, by being left to stand. In coagulation settling, an alkali, a coagulant or the like is added so as to precipitate the inhibitory substances, and these are separated by way of settling. Note that other pretreatments can also be performed in combination.

[0011] Meanwhile, in the nitrification step, the condensate demineralizer wastewater is

nitrified before or after being mixed with the flue gas desulfurization wastewater, so as to oxidize the ammoniacal nitrogen to nitrate-nitrogen (nitrite-nitrogen). For the nitrification, biological nitrification is performed by way of over-aeration in the presence of biological sludge containing nitrifying bacteria. Operations for nitrification steps in biological nitrification/denitrification methods that are commonly practiced in water treatment can be applied as-is in this step.

[0012] In terms of the biological sludge including nitrifying bacteria, nitrifying sludge can be collected from a system for performing biological nitrification/denitrification treatment and used as-is, but this can also be produced by returning biological sludge from the anaerobic treatment process described hereafter, mixing this with condensate demineralizer wastewater or mixed wastewater containing ammoniacal nitrogen and performing over-aeration. When over-aeration is performed in the presence of such biological sludge, the ammoniacal nitrogen is oxidized to nitrate-nitrogen (nitrite-nitrogen).

[0013] In the mixing step, the condensate demineralizer wastewater after nitrification is mixed with the flue gas desulfurization wastewater after pretreatment. If mixing is performed before nitrification, nitrification is performed after mixing. Either one may be first but all of the ammoniacal nitrogen should be oxidized to nitrate-nitrogen (nitrite-nitrogen) in the mixed state. The flue gas desulfurization wastewater is continuously discharged in substantially constant volumes, but condensate demineralizer wastewater is discharged once every 10 to 20 days, and therefore it is preferable that the condensate demineralizer wastewater be stored in a storage tank, and discharged and mixed with the flue gas desulfurization wastewater so as to average the flow rate.

[0014] In the anaerobic treatment step, the mixed wastewater after mixing and nitrification in this manner is contacted with the biological sludge including the denitrifying bacteria, in the anaerobic state, so as to perform denitrification and to reduce the selenium compounds.

[0015] The biological sludge used in the anaerobic treatment step is sludge including denitrifying bacteria, which is biological sludge produced by maintaining the mixed wastewater in an anaerobic state, and can be spontaneously generated by collecting biological sludge (activated sludge) in an anaerobic treatment method for wastewater, such as an activated sludge treatment method, adding this to the mixed wastewater and maintaining it in an anaerobic state. Denitrifying bacteria are predominant in such biological sludge, and the selenate (selenite) in the mixed wastewater is reduced by these denitrifying bacteria.

[0016] The denitrifying bacteria that can be used in the anaerobic treatment step are bacteria that break down organic matter using the oxygen from nitrate (nitrite) ions by way of nitric acid respiration, and are found among facultative anaerobic bacteria such as *Pseudomonas*. Such denitrifying bacteria are utilized in denitrification steps in denitrification methods based on nitrification/denitrification of ammoniacal nitrogen-containing wastewater using biological reactions. Denitrifying bacteria in such a biological denitrification methods can be directly used as the aforementioned denitrifying bacteria, and can also be spontaneously generated by collecting aerobic sludge (activated sludge) in an aerobic treatment method for wastewater, such as an activated sludge treatment method, and maintaining this in an anaerobic state in the presence of organic matter and nitrate (nitrite) ions.

[0017] Biological sludge containing such denitrifying bacteria is usually flocculent biological sludge, and in the present invention, flocculent biological sludge can be used as-is in a suspension, but it may also be used carried on a granular, fibrous or other high void-ratio carrier. There are no particular limitations on the carrier so long as it is capable of carrying biological sludge, but

sand, activated carbon, alumina gel, foamed plastic and the like can be mentioned. The biological sludge can be carried on the carrier by way of acclimatization, or treatment, in the presence of the carrier. Furthermore, bacteria that reduce selenate may be immobilized in a gel such as polyvinyl alcohol or polyethylene glycol.

[0018] In the anaerobic treatment step, as a result of contacting the mixed wastewater with biological sludge such as described above, in the anaerobic state, the nitrate-nitrogen (nitrite-nitrogen) in the mixed wastewater is reduced to nitrogen gas, to bring about denitrification, and the selenate (selenite), which is to say the Se^{6+} and/or Se^{4+} , is reduced and insolubilized. At this time, it is assumed that the Se^{6+} is reduced to Se^0 and/or Se^{2-} , via Se^{4+} . In the anaerobic treatment step, an anaerobic state means a state in which oxygen is cut off, but it is permissible for some amount of oxygen to be present, to an extent that does not impede reduction of the selenium compounds.

[0019] In the anaerobic treatment step described above, an oxygen source and a nutrient source are necessary for respiration in the biological sludge. Because this is in an anaerobic state, the oxygen source is not molecular oxygen, but rather the nitrate (nitrite) generated by nitrification is utilized. In terms of the nutrient source, organic matter contained in the mixed effluent and organic matter contained in the biological sludge can be utilized as substrates, but if these are not contained, methanol or the like is added separately. Consequently, high activity is maintained in the biological sludge, and this breakdown results in the reduction of the selenate (selenite).

[0020] In the case of mixed wastewater, the selenium compounds are reduced after the nitrate-nitrogen (nitrite-nitrogen) has been reduced, and it is necessary to add organic matter in the amounts required for these reductions. Because nitrate (nitrite) ions are present in such mixed wastewater, denitrifying bacteria appear in the biological sludge and the selenium reduction activity is kept high, whereby the selenate (selenite) is efficiently reduced.

[0021] The anaerobic treatment step described above is performed by introducing raw water and organic matter into an anaerobic treatment tank. An anaerobic treatment tank is used for contacting the mixed wastewater with the biological sludge, and any method can be adopted, such as a flotation method or a biofilm method. The flotation method is a method of bringing about contact by stirring flocculent biological sludge containing denitrifying bacteria in a floating state, which is performed in the same manner as the denitrifying step in biological denitrification methods. The biofilm method is a method in which the biological sludge is supported on a carrier so that a biofilm is formed and this is brought into contact with mixed wastewater, wherein systems such as fixed bed systems, fluidized bed systems or the like, or upward flow systems, downward flow systems or the like, similar to those used in the denitrifying step, can be used.

[0022] The residence time in the anaerobic treatment tank is the time necessary for reduction of the selenate (selenite) ions, but this can be regarded as the time required for decomposition of the organic matter present in the system, and if denitrification and the like is performed in the system, this can be set to no less than 1.1 times the time required for denitrification and the like. For the anaerobic treatment, the reaction is performed while maintaining a predetermined sludge concentration (500

to 50,000 mg/l, and preferably 2,000 to 20,000 mg/l) so that the aforementioned residence time is achieved.

[0023] When the selenium compound is reduced in the anaerobic treatment step described above, insoluble selenium compounds are formed and adsorbed on the biological sludge. The selenium compounds that have been adsorbed on the biological sludge are eliminated from the system by subjecting the biological sludge to solid-liquid separation in a solid-liquid separation step, and discharging it.

[0024] The anaerobic treatment solution taken from the aforementioned anaerobic treatment step contains excess added organic matter and other oxidizable matter, and an aerobic treatment step can be provided in order to oxidize and decompose these, as a post treatment following the anaerobic treatment step. Such aerobic treatment steps include activated sludge treatment steps and the like for breaking down excess organic matter that was used as a substrate in the anaerobic treatment step. Furthermore, an adsorption step using a resin for COD adsorption or the like can be provided in order to eliminate the COD that is not readily subject to biological decomposition.

[0025] When flue gas desulfurization wastewater is treated alone, it is necessary to add nitrate-nitrogen (nitrite-nitrogen) as an oxygen source, but when processing is performed in combination with condensate demineralizer wastewater, the nitrate-nitrogen (nitrite-nitrogen) contained therein can be used to keep the selenium removal activity high. Both of these types of wastewater are generated in thermal power plants, and therefore combined treatment is easy.

[0026] When Se content that is adsorbed on the biological sludge exceeds 20 wt% with respect to the MLSS, it will exhibit an inhibitory action on the biological sludge, but when flue gas desulfurization wastewater and condensate demineralizer wastewater generated in an ordinary thermal power plant are treated in combination, the Se content in the biological sludge will be 5 to 15 wt%, and thus a bioinhibitory action will not be exhibited.

[0027]

[Modes of Embodiment of the Invention] Hereafter, modes of embodiment of the present invention will be described based on the drawings. FIG. 1 (A) and (B) are system diagrams showing respectively different embodiments. In FIG. 1(A), in a pretreatment step 1, the flue gas desulfurization wastewater is subjected to pretreatment such as settling and/or coagulation settling, and in a mixing step 2, the condensate demineralizer wastewater is admixed. With the mixed wastewater, in a nitrification step 3, ammoniacal nitrogen is nitrified to nitrate-nitrogen (nitrite-nitrogen), and in an anaerobic treatment step 4, denitrification and selenium reduction and insolubilization are performed. In a solid-liquid separation step 5, the anaerobically treated solution is subjected to solid-liquid separation, and the sludge on which the selenium compounds have been adsorbed is discharged, while in a post-treatment step 6, the separated solution is subjected to post-treatment to produce treated water.

[0028] In FIG. 1 (B), after nitrifying the condensate demineralizer wastewater in a nitrification step 3, in a mixing step 2, this is mixed with the flue gas desulfurization wastewater that was subjected to pretreatment in a pretreatment step 1; then anaerobic treatment is performed in an anaerobic treatment step 4, solid-liquid separation is performed in a solid-liquid separation step 5, and post-treatment is performed in a post-treatment step 6.

[0029] In both of the above cases, if aerobic treatment is performed as a post-treatment in order to remove organic matter, solid-liquid separation may be performed in this aerobic treatment step, and the upstream solid-liquid separation step 5 may be omitted. The sludge separated in these solid-liquid separation steps can be returned to any of the nitrification step,

the anaerobic treatment step, or the aerobic treatment step, and a solid-liquid separation step can be provided at each step, in order to avoid dissolving the selenium.

[0030]

[Embodiments]

Example 1

Flue gas desulfurization wastewater discharged from a thermal power plant using coal as a fuel (pH 6.9, total Se: 2.76 mg/l, S_2O_6 : 109 mg/l, Fe: 212 mg/l, CODcr: 203 mg/l, SO_4^{2-} : 5800 mg/l, F: 55 mg/l) was subjected to settling treatment as a pretreatment step, 3 mg/l of Na_2CO_3 was added to the supernatant water for softening treatment, after which 250 mg/l of aluminum sulfate was added, and coagulation settling treatment was performed at a pH of 7.0. As a result, the Fe decreased to 0.9 mg/l and the F decreased to 8.4 mg/l, but almost no CODcr or Se was removed.

[0031] Next, 1/30 the amount of condensate demineralizer wastewater (NH_4-N : 800 mg/l) was added, and this was aerated in a 2 liter aeration tank (with a 3 liter settling basin) with a residence time of 6 hours, so as to perform nitrification. In this step, the pH was adjusted to pH 7.0 with a pH controller. This treated water was introduced into a 2 liter anaerobic tank (with 3 liter of settling basin), methanol was added at 4 times the amount of NO_3-N , anaerobic treatment was performed with a residence time of 12 hours, and denitrification and selenium reduction were performed. This was held in a re-aeration tank for post-treatment for 30 minutes. The MLSS in the anaerobic tank was maintained at 3500 to 4000 mg/l. As a result, the Se in the treated water reached 0.1 mg/l or less.

[0032]

[Effects of the Invention] With the present invention, biological nitrification and anaerobic treatment are performed with flue gas desulfurization wastewater and condensate demineralizer wastewater combined, so that the ammoniacal nitrogen in the condensate demineralizer wastewater can be used to keep the selenium removal activity of the biological sludge high, whereby the selenium in the flue gas desulfurization waste water can be efficiently removed, and the ammoniacal nitrogen in the condensate demineralizer wastewater can also be efficiently removed, allowing both types of wastewater to be efficiently treated at low cost.

[Brief Description of the Drawings]

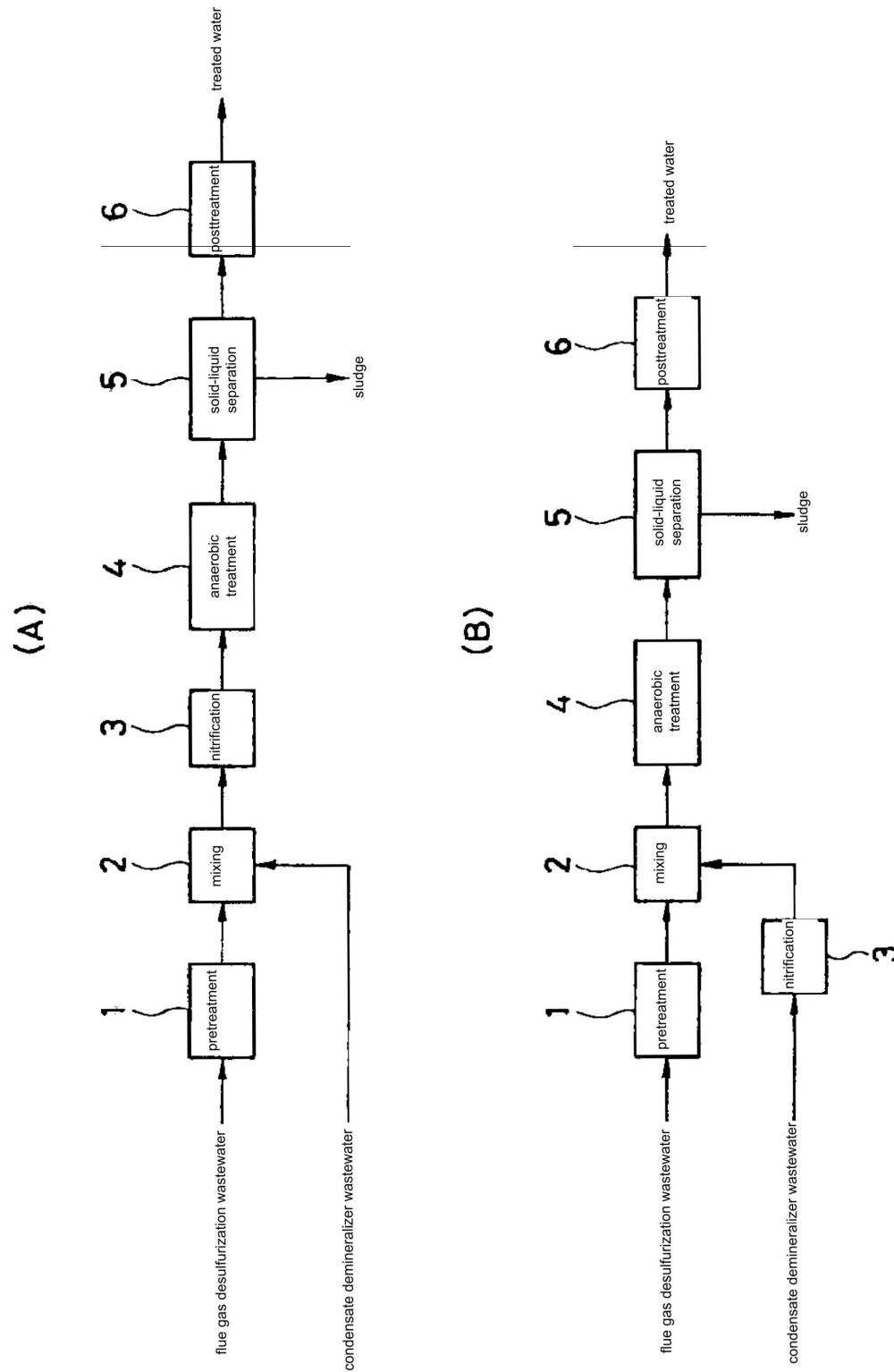
[FIG. 1] (A) and (B) are system diagrams showing respectively different embodiments.

[Explanation of the Symbols]

- 1 pretreatment step
- 2 mixing step
- 3 nitrification step
- 4 anaerobic treatment step
- 5 solid-liquid separation step
- 6 post-treatment step

(5)

[FIG. 1]



[Amendment to Proceedings]

[Submission Date] August 1, 1995

[Amendment to Proceedings 1]

[Name of Document to Be Amended] Drawings

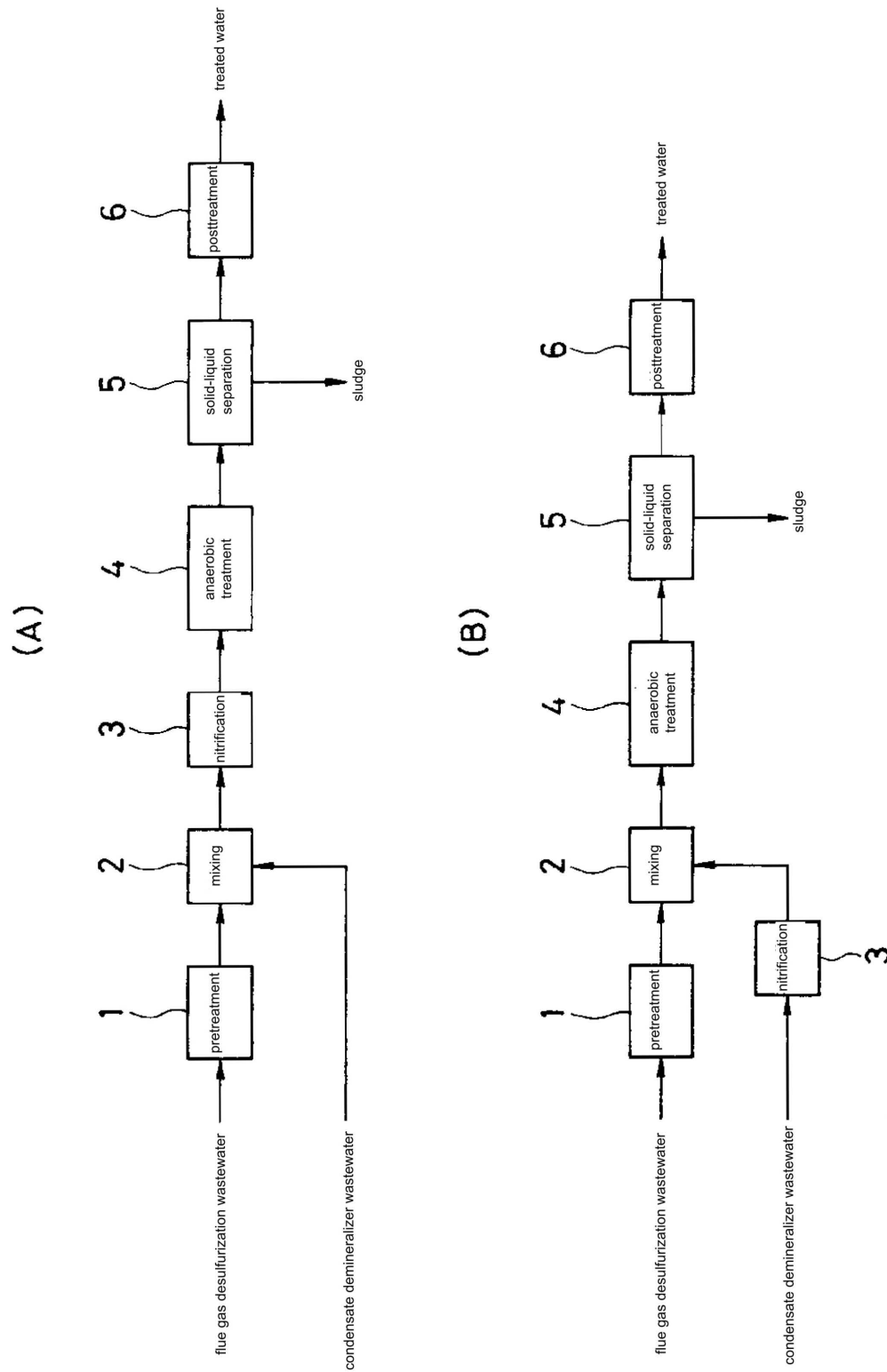
[Name of Item to Be Amended] All figures

[Amendment Method] modification

[Content of the Amendment]

(7)

[FIG. 1]



Certification of Translation

Translator's Declaration: May 16, 2017

I, Martin Cross, hereby declare:

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

- over 25 years as a Japanese-English translator focusing primarily on patents, and technical and scientific documents;
- co-author of the *Japanese Patent Translator's Handbook*, published by American Translators Association;
- United States district court recognition as an expert in Japanese technical translation for patent litigation; and
- B.A. in English Literature, from York University, courses in Chemistry and Organic Chemistry from Thompson Rivers University.

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-09-038694-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.

Martin Cross

