

WATER TREATMENT METHOD AND WATER TREATMENT APPARATUS

TECHNICAL FIELD

[0001] Embodiments described herein relate generally to a water treatment method and a
5 water treatment apparatus.

BACKGROUND

[0002] Nowadays, effective utilization of water resources is demanded due to industrial
development and population growth. In order to realize the effective utilization of water
10 resources, it is important to reuse various types of wastewater such as industrial wastewater and
domestic wastewater, by performing purification.

[0003] In order to purify wastewater, there is a need to separate and remove
water-insoluble matters and impurities contained in water. As a method of purifying
wastewater, there can be cited, for example, a membrane separation method, a centrifugal
15 separation method, an activated carbon adsorption method, an ozone treatment method, and a
method of removal through sedimentation of suspended substances performed by adding an
aggregating agent. By using these water treatment methods, chemical substances which exert
large influences on environments such as phosphorus and fluorine contained in wastewater can
be removed, and further, oils, clays and the like dispersed in water can be removed.

[0004] As a method of removing harmful fluorine-based substances from
fluorine-containing wastewater, a method of using a calcium agent or an aluminum agent has
been well-known conventionally, and it is often the case where fluoroborate ions (BF_4^-) bonded
to boron, other than fluoride ions, exist in wastewater in glass industry and the like. As a
method of removing the fluoroborate ion, a method of decomposing the ion by using an
25 aluminum compound, a method of adsorbing the ion by using a chelate resin or the like, are
known.

[0005] For example, as a method of decomposing the fluoroborate ion by using the
aluminum compound, Patent Reference 1 proposes a method in which an aluminum compound

is added to a tetrafluoroborate ion so that the ion is converted into an aluminum fluoride ion, and the ion is separated through sedimentation as fluoride salt of calcium aluminate. Further, as a method of removing the fluoroborate ion by using a glucamine (aminopolyalcohol)-based chelate resin, there are known a method described in Patent Reference 2 in which an

5 aminopolyol-based chelate adsorbent and a fluorine adsorbent are used in combination, and a method described in Patent Reference 3 in which an aminopolyol-based chelate resin is used to decompose a fluoroborate ion, and thereafter, treatment solution is evaporated to be concentrated.

[0006] However, in the method described in Patent Reference 1, a large amount of
10 aluminum compound is required, and a large amount of sludge is generated, so that there is a problem that a treatment cost for wastewater is increased in conjunction with an increase in an agent cost and an increase in a treatment cost for the sludge. In the method described in Patent Reference 2, since the fluoride ion and the tetrafluoroborate ion are adsorbed at the same time, there is a problem that a purity of the collected substance is lowered, and since the fluoride ion
15 acts as an inhibitor when the tetrafluoroborate ion is adsorbed by the aminopolyol-based chelate resin, there is a problem that an adsorption rate of the tetrafluoroborate ion is decreased.

Further, in Patent Reference 3, the decomposition of the tetrafluoroborate ion is facilitated by the adsorption of boron in the water, but, this method has a problem that a rate of decomposition of borofluoride is limited, and thus a prompt removal cannot be conducted.

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RELEVANT REFERENCES

PATENT REFERENCE

[0007] Patent Reference 1: JP-A 60-000117

Patent Reference 2: JP-A 2-099189

25 Patent Reference 3: JP-B2 3915176

SUMMARY

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] A problem to be solved by the present invention is to remove, from wastewater containing fluorine ions and tetrafluoroborate ions as fluorine-based substances, the fluorine ions and the tetrafluoroborate ions efficiently and effectively at a low cost.

MEANS FOR SOLVING THE PROBLEMS

5 [0009] A water treatment method of an embodiment is a treatment method of wastewater containing fluoride ions and tetrafluoroborate ions, the method including: a first step of adding a water-insoluble calcium-containing inorganic substance to the wastewater in a reaction tank to convert the fluoride ions contained in the wastewater into calcium fluoride; and a second step of enabling solid-liquid separation of the wastewater containing the calcium fluoride in a
10 solid-liquid separation tank, and removing the calcium fluoride from the wastewater to obtain first treated water. The method further includes: a third step of adding a pH regulator to the first treated water in a pH regulating tank to regulate a pH of the first treated water to an acidic region; and a fourth step of passing the first treated water through a container filled with aminopolyol-based chelate resins, and adsorbing and removing the tetrafluoroborate ions from
15 the first treated water to obtain second treated water.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] [FIG. 1] is a schematic configuration diagram of a water treatment apparatus in a first embodiment.

20 [FIG. 2] is a schematic configuration diagram of a water treatment apparatus in a second embodiment.

DETAILED DESCRIPTION

[0011] (First embodiment)

25 FIG. 1 is a diagram illustrating a schematic configuration of a water treatment apparatus of the present embodiment. A water treatment apparatus 10 illustrated in FIG. 1 has: a reaction tank 11 for removing fluoride ions in water to be treated W0 such as wastewater; a solid-liquid separation tank (planar filtering device) 12 positioned at a downstream side of

the reaction tank 11, including a filter 121 having a surface horizontal to a mounting surface, and having an inner space which is vertically divided into 12A and 12B by the filter 121; a pH regulating tank 13 positioned at a downstream side of the solid-liquid separation tank 12, and used for performing pH regulation of primary treated water W1 obtained by removing the fluoride ions from the water to be treated W0; and a resin column 14 for removing tetrafluoroborate ions remained in the primary treated water W1.

[0012] The reaction tank 11 is used for adding a water-insoluble calcium-containing inorganic substance to the water to be treated W0 to convert the fluoride ions contained in the water to be treated W0 into calcium fluoride, and the solid-liquid separation tank (planar filtering device 12) is used for enabling solid-liquid separation of the water to be treated W0 containing the calcium fluoride, and removing the calcium fluoride from the water to be treated W0 to obtain the primary treated water W1. Further, the pH regulating tank is used for adding a pH regulator to the primary treated water W1 to regulate a pH of the primary treated water W1 to an acidic region, and the resin column 14 is a container filled with aminopolyol-based chelate resins, used for passing the primary treated water therethrough, and adsorbing and removing the tetrafluoroborate ions from the primary treated water W1 to obtain secondary treated water W2.

[0013] Note that since the filter 121 in the solid-liquid separation tank 12 is made to be horizontal to the mounting surface, a water passage direction and a direction of gravity applied to the water to be treated W0 coincide with each other, so that a layer of solid matter mainly formed of calcium fluoride being a removal target substance converted in the reaction tank 11, is uniformly formed on the filter 121. The layer of calcium fluoride functions as a filter layer with respect to calcium fluoride in the water to be treated W0 which is passed later or continuously passed, so that even when a fine precipitate of calcium fluoride (reaction product) exists in the water to be treated W0, the precipitate can be collected and removed.

[0014] Although the filter 121 can be formed of, for example, a filter cloth, a metal mesh, a porous ceramic, a porous polymer or the like, one formed of the filter cloth is particularly preferable, and the filter cloth made of, for example, polypropylene, nylon, polyester or the like,

and woven by double-weaving, twill-weaving, plain-weaving, satin-weaving or the like is used. Among the above, if a soft filter cloth, a polymeric microfiltration membrane (MF membrane) or the like is used, it is possible to preferably capture calcium fluoride which is generated for removing fluorine ions, as will be described below.

5 [0015] Note that the solid-liquid separation tank 12 of the present embodiment is not limited to the above-described configuration, and it can be configured with an ordinary filter.

[0016] Further, in the resin column 14, aminopolyol-based chelate resins R whose average particle diameter is 0.45 to 0.6 mm, for example, are filled. The aminopolyol-based chelate resin R is, for example, a N-methyl glucamine-type chelate resin, and as the resin, there can be
10 concretely cited DIAION CBR-03, CBR-05 manufactured by Mitsubishi Chemical Corporation, Chelest Fiber GRY-L manufactured by Chelest Corporation and the like, in addition to Amberlite IRA-743 (trade name) manufactured by Rohm & Haas Company.

[0017] Note that the above-described average particle diameter can be measured by laser diffractometry, for example, and concretely, it can be measured with a SALD-3100
15 measurement apparatus (trade name) manufactured by Shimadzu Corporation, or the like. Note that in the following description, when the term “average particle diameter” appears and a concrete numeric value thereof is described, the “average particle diameter” indicates one measured by the laser diffractometry as described above, unless described otherwise.

[0018] The reaction tank 11 and the solid-liquid separation tank 12 are connected by a
20 pipe 22 via a pump 31, and the solid-liquid separation tank 12 and the pH regulating tank 13 are connected by a pipe 23. Note that it is also possible to dispose a not-illustrated pump on the pipe 23. Further, the pH regulating tank 13 and the resin column 14 are connected by a pipe 24. Further, in the upper part 12A of the solid-liquid separation tank 12, there are disposed a pipe 26 and a pipe 27, which form a washing water supply line and
25 a waste liquid discharge line, respectively.

[0019] Although a container shape, a capacity, a material and the like of the reaction tank 11 are not particularly limited, the reaction tank 11 preferably has a capacity such that a storage time of at least 15 minutes can be secured. Further, it is preferable to provide a

baffle plate or the like in the reaction tank 11 so that a shortcut of the water to be treated W0 from a supply port toward the pipe 22 can be prevented.

[0020] Further, in the reaction tank 11 and the pH regulating tank 13, an agitator 111 and an agitator 131 are provided.

5 [0021] Next, a water treatment method using the water treatment apparatus 10 illustrated in FIG. 1 will be described. First, as the water to be treated W0, wastewater containing fluoride ions and tetrafluoroborate ions is supplied into the reaction tank 11 through the pipe 21 being a water supply line, and a water-insoluble calcium-containing inorganic substance is added into the reaction tank 11, thereby converting the fluoride ions contained in
10 the water to be treated W0 into calcium fluoride in the reaction tank 11. At this time, the water to be treated W0 and the calcium-containing inorganic substance in the reaction tank 11 are mixed by the agitator 111.

[0022] In the present embodiment, the term “water-insoluble calcium-containing inorganic substance” indicates a calcium-containing inorganic substance whose solubility in water is 10 g
15 or less per 1000 ml (at 25°C).

[0023] Further, as the calcium-containing inorganic substance, a substance which does not have a hydrate or hydroxyl group is preferable. This is because a substance having the hydrate or hydroxyl group has a characteristic that it is softer than the other substances, and thus is sometimes clogged in a hole of filter.

20 [0024] Concretely, there can be cited a natural ore such as aragonite, ulexite, merrillite, omphacite, uvarovite, scheelite, perovskite, hedenbergite, zoisite, apophyllite, dolomite, creedite, piemontite, spurrite, gypsum dihydrate, titanite, charoite, anorthite, diopside, hedenbergite, johannsenite, tremolite, rhodonite, pigeonite, hornblende, augite, pectolite, vesuvianite, henmilite, calcite, aragonite, montmorillonite, actinolite, epidote, clinozoisite, and apatite.

25 Further, there can be cited a calcium compound obtained through synthesis and generation steps, such as calcium carbonate, calcium sulfite, calcium hydroxide, calcium sulfate, calcium titanate, and calcium tungstate.

[0025] Among the above, calcium carbonate whose solubility in water is low, and the ore

containing calcium carbonate as its main component (aragonite or dolomite, for example) are preferable, and calcium carbonate which does not generate anions other than fluoride ions and tetrafluoroborate ions to be removed, is particularly preferable. Excessive ions decrease an adsorption rate of tetrafluoroborate ions in the resin column 14 to be described below, and thus
5 deteriorate a removal efficiency of the tetrafluoroborate ions.

[0026] Further, in a case where calcium chloride is used as the above-described calcium-containing inorganic substance, although calcium fluoride is generated in the same manner in the treatment of fluoride ions, chloride ions are generated, by way of compensation, in the water to be treated W0. For this reason, a problem regarding a corrosion of pipe and the
10 like sometimes arises. Further, the generation of chloride ions becomes a cause of decreasing the adsorption rate in the resin column 14 at the post-stage, resulting in that a cost of the water treatment method of the present embodiment is increased.

[0027] It is preferable to use the calcium-containing inorganic substance as described above, having particles whose average particle diameter is 2 to 50 μm . If the average particle
15 diameter becomes large such that it exceeds 50 μm , a surface area of the calcium-containing inorganic substance becomes small, resulting in that a reaction rate when the above-described fluoride ion is converted into calcium fluoride is sometimes decreased. If the average particle diameter is smaller than 2 μm , a diameter of generated calcium fluoride becomes small, and it becomes sometimes difficult to collect the calcium fluoride in the solid-liquid separation tank
20 12 as will be described below.

[0028] In order to obtain the calcium-containing inorganic substance with the average particle diameter described above, a classification is appropriately conducted. When the particle diameter of the acquired calcium-containing inorganic substance is larger than the above-described average particle diameter, a grinding is performed by using a ball mill, a
25 Henschel mixer, a roller or the like.

[0029] Note that when the fluoride ion in the water to be treated W0 is reacted with calcium in the calcium-containing inorganic substance to be converted into calcium fluoride in the reaction tank 11, it is preferable to add a pH regulator into the reaction tank 11 to set a pH of the

water to be treated W0 in the reaction tank 11 to fall within a range of 2 to 4. This makes it possible to facilitate the above-described reaction, and to facilitate the conversion of fluoride ion into calcium fluoride. Note that the pH regulator added in the reaction tank 11 is sometimes referred to as “additional pH regulator” so that it can be distinguished from a pH regulator added in the pH regulating tank 13, which will be described later.

[0030] As the above-described additional pH regulator, there can be cited sulfuric acid, nitric acid, organic acid, hydrogen halide excluding hydrogen fluoride, and the like. Among the above, sulfuric acid is particularly preferable. This is because sulfuric acid is turned into a sulfate ion in the water to be treated W0, and the sulfate ion reacts with a calcium ion of the calcium-containing inorganic substance to be calcium sulfate having a relatively small solubility, resulting in that an excessive ion is solidified.

[0031] Note that if hydrogen fluoride is used as the additional pH regulator, there is a case where fluoride ions are generated, and the fluoride ions become excessive, which decreases the adsorption rate of tetrafluoroborate ions in the resin column 14, and lowers the removal efficiency of the tetrafluoroborate ions.

[0032] Next, the pump 31 is driven to transfer the water to be treated W0 in a slurry state containing the generated calcium fluoride, onto the filter 121 of the solid-liquid separation tank 12 via the pipe 22, and the water to be treated W0 is passed through the filter 121. Accordingly, a large part of calcium fluoride is collected and removed from the water to be treated W0 in the slurry state, resulting in that a concentration of fluoride ions in the primary treated water W1 obtained by passing the water to be treated W0 through the filter 121, is reduced up to 30 mg/L or less, for example.

[0033] Further, in the present embodiment, the planar filtering device including the filter 121 having the surface horizontal to the mounting surface, is used as the solid-liquid separation tank 12 as described above, so that a layer of solid matter mainly formed of calcium fluoride being a removal target substance is formed on the filter 121. The layer functions as a filter layer with respect to calcium fluoride in the water to be treated W0 which is passed later or continuously passed, so that even when a fine precipitate of calcium fluoride (reaction product)

exists in the water to be treated W0, the precipitate can be collected and removed.

[0034] Meanwhile, when the filtration progresses to some extent, a thickness of the above-described layer formed on the filter 121 is increased to lower a filtration rate. When such a state is created, the supply of the water to be treated W0 via the pipe 22 is stopped, washing water is supplied from the pipe 26 being the washing water supply line to wash off the solid matter on the filter 121, and waste liquid of concentrated slurry containing the solid matter is discharged from the pipe 27 being the waste liquid discharge line. Thereafter, the water to be treated W0 is transferred again onto the filter 121 via the pipe 22 and passed through the filter 121, and the collection and the removal of calcium fluoride in the water to be treated W0 are conducted to obtain the primary treated water W1, in a manner similar to the above.

[0035] Note that although it is also possible to add an aggregating polymer in the reaction tank 11 to improve a collection efficiency of calcium fluoride in the solid-liquid separation tank 12, such an aggregating polymer remains in the water to be treated W0, so that there is a possibility that a gap formed between the filled aminopolyol-based chelate resins is clogged with the aggregating polymer in the resin column 14 at the post-stage, to shorten an operating life of the resin column 14. Further, when the aggregating agent is used, the agent cost is required, and further, a cost for treating a sludge being a sediment is generated, resulting in that a cost of water treatment in the present embodiment is increased.

[0036] Next, the primary treated water W1 obtained by the solid-liquid separation tank 12 is introduced into the pH regulating tank 13 via the pipe 23. At this time, it is also possible to design such that a pump is disposed on the pipe 23 according to need, and by utilizing a delivery force of the pump, the primary treated water W1 is introduced into the pH regulating tank 13 via the pipe 23.

[0037] Since the calcium-containing inorganic substance such as calcium carbonate is added in the reaction tank 11, a pH value of the primary treated water W1 is in a neutral region of a range of 6 to 8, so that in the pH regulating tank 13, the pH regulator is added to regulate the pH value of the primary treated water W1 to be in an acidic region of preferably 2 to 4. This is for realizing chelation of the tetrafluoroborate ions contained in the primary treated

water W1 performed by the aminopolyol-based chelate resins in the resin column 14 to be described below.

[0038] Note that sulfuric acid is preferable as the above-described pH regulator. Further, the primary treated water W1 and the pH regulator are sufficiently mixed by the agitator 131.

5 [0039] Next, a pump 32 is driven to introduce the pH-regulated primary treated water W1 into the resin column 14 via the pipe 24, and the water is passed through gaps between the aminopolyol-based chelate resins R filled in the resin column 14. At this time, the aminopolyol-based chelate resin R causes a complexation reaction with the tetrafluoroborate ion contained in the water to be treated W1, resulting in that the tetrafluoroborate ion is taken into
10 the aminopolyol-based chelate resin as a complex ion to form a complex. As a result of this, the tetrafluoroborate ion in the primary treated water W1 is adsorbed by the aminopolyol-based chelate resin, and by removing the tetrafluoroborate ions from the primary treated water W1, secondary treated water W2 is obtained.

[0040] Note that the secondary treated water W2 is discharged to the outside through a pipe
15 25 disposed under the resin column 14. The secondary treated water W2 does not contain harmful fluoride ions and tetrafluoroborate ions, so that it can be directly supplied for reuse as water resource.

[0041] As described above, by conducting the process of the conversion reaction in the reaction tank 11 and the collection in the solid-liquid separation tank 12, the fluoride ions are
20 already removed from the primary treated water W1 to be introduced into the resin column 14, so that when the primary treated water W1 is introduced into the resin column 14, there is no chance that the tetrafluoroborate ions contained in the primary treated water W1 are inhibited by the presence of fluoride ions. Therefore, it is possible to increase the adsorption rate of the tetrafluoroborate ions adsorbed by the aminopolyol-based chelate resins R.

25 [0042] Further, since no aggregating agent is used, the agent cost is not required, and the cost for treating the sludge being the sediment is also not generated.

[0043] Consequently, according to the present embodiment, it is possible to remove, from the water to be treated W0 containing fluorine ions and tetrafluoroborate ions, the fluorine ions

and the tetrafluoroborate ions efficiently and effectively at a low cost.

[0044] Note that when the primary treated water W1 is continuously passed through the resin column 14, and the adsorption rate of tetrafluoroborate adsorbed by the aminopolyol-based chelate resins R starts to be decreased, the supply of the primary treated water W1 is stopped, and desorption liquid is supplied into the resin column 14 via a pipe 28, to thereby desorb tetrafluoroborate adsorbed in the aminopolyol-based chelate resins. There is no problem in particular if the desorption liquid can alkalify the inside of the resin column 14, and aqueous solution of sodium hydroxide is preferably used as the desorption liquid. The wastewater containing the tetrafluoroborate ions desorbed by the desorption liquid is discharged to the outside of the resin column 14 via a pipe 29, and stored in a not-illustrated waste alkali tank.

[0045] By performing the treatment as above, the aminopolyol-based chelate resins filled in the resin column 14 recover adsorption capabilities, so that by supplying the primary treated water W1 again via the pipe 24, it is possible to adsorb the tetrafluoroborate ions in the primary treated water W1 in the resin column 14 again to obtain the secondary treated water W2 as a result of removing the tetrafluoroborate ions.

[0046] (Second embodiment)

FIG. 2 is a diagram illustrating a schematic configuration of a water treatment apparatus of the present embodiment. Note that components which are the same as or similar to those of the water treatment apparatus 10 illustrated in FIG. 1 are denoted by the same reference numerals.

[0047] A water treatment apparatus 40 illustrated in FIG. 2 is different from the water treatment apparatus 10 illustrated in FIG. 1 in a point that the filter 121 in the solid-liquid separation tank 12 is changed to a horizontal filter cloth 122 capable of being wound by rollers 123, and a pipe (compressed air supply line) 46 for introducing compressed air and a container 16 are disposed instead of the pipe 26 introducing the washing water and the like, and the other configuration thereof is similar to that of the water treatment apparatus 10. Therefore, description will be made hereinafter by focusing attention on a point of difference of water treatment method based on the above-described difference of the apparatus, with respect to the

first embodiment.

[0048] Note that the above-described “horizontal filter cloth” means that the filter cloth is disposed horizontally with respect to the mounting surface of the solid-liquid separation tank 12.

5 [0049] In the present embodiment, the water to be treated W0 in the slurry state containing calcium fluoride obtained by converting the fluoride ions by adding the calcium-containing inorganic substance in the reaction tank 11, is supplied onto the filter cloth 122 of the solid-liquid separation tank 12. At this time, calcium fluoride contained in the water to be treated W0 is collected by the filter cloth 122, and a layer of solid matter mainly formed of
10 calcium fluoride being a removal target substance is formed on the filter cloth 122.

[0050] As described above, the aforementioned layer functions as a filter layer with respect to calcium fluoride in the water to be treated W0 which is passed later or continuously passed, so that even when a fine precipitate of calcium fluoride (reaction product) exists in the water to be treated W0, the precipitate can be collected and removed.

15 [0051] However, when a period of time of water passage becomes long and a thickness of the above-described layer is increased, the filtration rate is lowered. When such a state is created, the supply of the water to be treated W0 via the pipe 22 is stopped, and the compressed air is blown onto the filter cloth 122 via the pipe 46 being the compressed air supply line. This makes it possible to facilitate the passage of the water to be treated W0 remained on the filter
20 cloth 122, through the filter cloth 122, and to decrease a water content of the aforementioned layer formed on the filter cloth 122.

[0052] The water to be treated W0 passed through the filter cloth 122 is sequentially transferred to the pH regulating tank 13 and the resin column 14, as the primary treated water W1, and the tetrafluoroborate ions in the primary treated water W1 are removed, as described in
25 the first embodiment. Meanwhile, regarding the filter cloth 122, a not-illustrated air cylinder or the like is used to lift an upper part of the solid-liquid separation tank 12, and then by rotating the rollers 123, the above-described layer remained on the filter cloth 122 is scraped off by using a not-illustrated scraper or the like, and housed in the container 16.

[0053] Note that after the layer of solid matter mainly formed of calcium fluoride on the filter cloth 122 is removed, the rollers 123 are rotated to dispose a new filter cloth 122, and the upper part of the solid-liquid separation tank 12 is returned to its original position. Thereafter, the water to be treated W0 is transferred again onto the filter cloth 122 via the pipe 22 and passed through the filter cloth 122, and the collection and the removal of calcium fluoride in the water to be treated W0 are conducted to obtain the primary treated water W1, in a manner similar to the above.

[0054] In the present embodiment, washing water is not used for washing the layer of solid matter formed on the filter cloth 122, so that a water recovery ratio in the treatment of the water to be treated W0 is improved.

[0055] Further, in a similar manner to the first embodiment, when the primary treated water W1 is introduced into the resin column 14, there is no chance that the tetrafluoroborate ions contained in the primary treated water W1 are inhibited by the presence of fluoride ions, so that it is possible to increase the adsorption rate of the tetrafluoroborate ions adsorbed by the aminopolyol-based chelate resins R. Further, since no aggregating agent is used, the agent cost is not required, and the cost for treating the sludge being the sediment is also not generated.

[0056] Consequently, according to the present embodiment, it is possible to remove, from the water to be treated W0 containing fluorine ions and tetrafluoroborate ions, the fluorine ions and the tetrafluoroborate ions efficiently and effectively at a low cost.

EXAMPLES

[0057] (Example 1)

A test was conducted by using the water treatment apparatus 10 illustrated in FIG. 1.

Wastewater containing fluoride ions of about 1000 mg/L, and tetrafluoroborate ions of about

200 mg/L was used as the water to be treated W0, the water to be treated W0 was supplied to the reaction tank, the pH of the water was regulated to 3 by sulfuric acid, and after that, powders of calcium carbonate having an average particle diameter of 40 μm were added in an amount of 0.75 times the amount of the fluoride ions in a mole ratio, and the water and the powders were

mixed for 15 minutes by the agitator 111. Thereafter, the pump 31 was used to supply the mixture to the solid-liquid separation tank 12 formed of a horizontal filtering device in which a filter cloth made of polypropylene with a hole diameter of 10 μm was set, to thereby perform solid-liquid separation. Regarding ion concentrations of the primary treated water W1, the concentration of fluoride ions was 15 mg/L, and the concentration of tetrafluoroborate ions was about 180 mg/L. Further, a solid content in the water was less than 1 mg/L.

[0058] Next, the pH of the primary treated water W1 was regulated to 3 by sulfuric acid in the pH regulating tank 13, and after that, the water was passed through the resin column 14 filled with chelate resins carrying N-methyl glucamine being aminopolyol (trade name (CRB-05), manufactured by Mitsui Chemicals, Inc.), and the concentration of tetrafluoroborate ions discharged from the pipe 25 was analyzed.

[0059] When a removal performance of the tetrafluoroborate ions was checked by changing a passage water quantity SV, the tetrafluoroborate ion was not detected up to when SV reached 40, and at SV50, a very small amount of tetrafluoroborate ion was detected. Accordingly, it was clarified that the treatment amount of the water treatment apparatus 10 corresponds to SV40 with respect to the above-described resin column 14.

[0060] (Comparative Example 1)

A test was conducted in a similar manner to the example 1 except that calcium chloride, instead of calcium carbonate, was used. Note that a particle diameter of calcium fluoride generated at this time was too small so that the solid-liquid separation could not be performed in the solid-liquid separation tank 12, and thus the filtration was conducted after forming a floc by adding a small amount of aggregating polymer into the reaction tank 11. Regarding ion concentrations of the primary treated water W1, the concentration of fluoride ions was 13 mg/L, and the concentration of tetrafluoroborate ions was about 180 mg/L. Further, a solid content in the water was less than 1 mg/L.

[0061] When the water was subjected to the pH regulation with the use of sulfuric acid, and then passed through the resin column 14 in a similar manner, the tetrafluoroborate ion was not detected up to when SV reached 5, but, the ion was detected at SV10. Accordingly, it was

clarified that the treatment amount of the water treatment apparatus 10 corresponds to SV5 with respect to the above-described resin column 14.

[0062] (Comparative Example 2)

The water to be treated W0 was directly supplied to the pH regulating tank 13, and passed
5 through the resin column 14 without being treated with calcium-containing solid, it was not possible to remove the tetrafluoroborate ion even at SV2.

[0063] While several embodiments of the present invention have been described above, these embodiments have been presented by way of example, and are not intended to limit the scope of the inventions. The novel embodiments described herein may be
10 implemented in a variety of other forms, and various omissions, substitutions and changes thereof may be made without departing from the spirit of the inventions. Such embodiments and modifications are included in the scope and spirit of the invention, and also included in the inventions described in the accompanying claims and their equivalents.

15 EXPLANATION OF NUMERALS

[0064] 10, 40 water treatment apparatus; 11 reaction tank; 111 agitator; 12 solid-liquid separation tank; 121 filter; 122 horizontal filter cloth (capable of being wound); 13 pH regulating tank; 131 agitator; 14 column filled with aminopolyol-based chelate resins; 16 container; W0 water to be treated; W1 primary
20 treated water; W2 secondary treated water; R aminopolyol-based chelate resin; 21 to 29, 46 pipe; 31, 32 pump.

CLAIMS

1. A water treatment method being a treatment method of wastewater containing fluoride ions and tetrafluoroborate ions, the water treatment method comprising:
 - 5 a first step of adding a water-insoluble calcium-containing inorganic substance to the wastewater in a reaction tank to convert the fluoride ions contained in the wastewater into calcium fluoride;
 - a second step of enabling solid-liquid separation of the wastewater containing the calcium fluoride in a solid-liquid separation tank, and removing the calcium fluoride from the
10 wastewater to obtain first treated water;
 - a third step of adding a pH regulator to the first treated water in a pH regulating tank to regulate a pH of the first treated water to an acidic region; and
 - a fourth step of passing the first treated water through a container filled with aminopolyol-based chelate resins, and adsorbing and removing the tetrafluoroborate ions from
15 the first treated water to obtain second treated water.
2. The water treatment method according to claim 1,
wherein, in the first step, an additional pH regulator is added into the reaction tank to regulate the pH of the wastewater to the acidic region.
3. The water treatment method according to claim 1 or 2,
20 wherein the solid-liquid separation device is a horizontal filtering device.
4. The water treatment method according to any one of claims 1 to 3,
wherein the calcium-containing inorganic substance is calcium carbonate.
5. The water treatment method according to any one of claims 1 to 4,
wherein the pH regulator is sulfuric acid.
- 25 6. The water treatment method according to any one of claims 2 to 5,
wherein the additional pH regulator is sulfuric acid.
7. The water treatment method according to any one of claims 1 to 6, further comprising

a fifth step of supplying alkaline desorption liquid into the container to desorb the tetrafluoroborate ions adsorbed in the aminopolyol-based chelate resins.

8. The water treatment method according to claim 7,
wherein the desorption liquid is aqueous solution of sodium hydroxide.

5 9. A water treatment apparatus being a treatment apparatus of wastewater containing fluoride ions and tetrafluoroborate ions, the water treatment apparatus comprising:
a reaction tank for adding a water-insoluble calcium-containing inorganic substance to the wastewater to convert the fluoride ions contained in the wastewater into calcium fluoride;
a solid-liquid separation tank for enabling solid-liquid separation of the wastewater
10 containing the calcium fluoride, and removing the calcium fluoride from the wastewater to obtain first treated water;

a pH regulating tank for adding a pH regulator to the first treated water to regulate a pH of the first treated water to an acidic region; and

a container filled with aminopolyol-based chelate resins, used for passing the first
15 treated water therethrough, and adsorbing and removing the tetrafluoroborate ions from the first treated water to obtain second treated water.

10. The water treatment apparatus according to claim 9,
wherein the solid-liquid separation device is a horizontal filtering device.