

## DESCRIPTION

### TITLE

#### AMMONIA-CONTAINING WASTEWATER TREATMENT APPARATUS AND TREATMENT METHOD

### TECHNICAL FIELD

[0001]

The present invention relates to an ammonia-containing wastewater treatment  
apparatus and a treatment method for treating ammonia-containing wastewater discharged  
from electronic industry plants, chemical plants, and other facilities, and recovering the  
ammonia contained in wastewater as ammonium sulfate.

### BACKGROUND

[0002]

Ammonia-containing wastewater having a relatively high concentration that is  
discharged from electronic industry plants such as semiconductor plants, chemical plants,  
thermal power plants, for example, is treated by ammonia stripping (see Patent Document  
1, for example), graduation (see Patent Document 2, for example), catalytic wet oxidation  
(see Patent Document 3, for example), and other methods. Ammonia-containing  
wastewater having a relatively low concentration is treated by biological treatment, for  
example.

[0003]

In ammonia stripping, after adding an alkali solution to ammonia-containing  
wastewater, the ammonia-containing wastewater is warmed and allowed to flow through a  
stripping tower filled with a filler and is brought into contact with vapor and air, and thus  
ammonia in the wastewater is moved to the gas side. This process is relatively simple but  
needs a large-size stripping tower. This process further requires treatment of the

ammonia, which has been moved to the gas side using thermal energy such as heating or vapor, by catalytic oxidation at high temperatures, raising a problem of increased costs for treatment. Also,  $\text{NO}_x$ ,  $\text{N}_2\text{O}$ , or other substances may be generated during the catalytic oxidation.

5 [0004]

With the graduation process, ammonia-containing wastewater is heated and vaporized to produce ammonia-containing vapor, which then undergoes condensation and is recovered as ammonia water. This process has disadvantages including energy costs for warming to produce vapor, adhesion of scales to a heating surface of an evaporator, and  
10 the like.

[0005]

The catalytic wet oxidation is a process for treating ammonia-containing wastewater at 100 to 370°C under pressure in the presence of a catalyst. This treatment process, which is performed under high temperatures and high pressures, raises safety and  
15 cost issues.

[0006]

A vapor-liquid separation membrane method has been proposed for removing ammonia from ammonia-containing wastewater using a hydrophobic porous vapor-liquid separation membrane which allows passage of ammonia but prohibits passage of liquid  
20 (see Patent Document 4, for example). According to this method, ammonia-containing wastewater is alkalized to have a pH 10 or higher and the ammonia within the wastewater is gasified, and the vapor-liquid separation membrane is sucked on the downstream side by a vacuum pump, thereby removing the ammonia from the ammonia-containing wastewater. This method, however, requires installation of a separate ammonium sulfate scrubber.

25 [0007]

A further vapor-liquid separation membrane method has also been proposed for bringing a sulfuric acid solution flowing on the downstream side of a hydrophobic hollow fiber membrane, which is a vapor-liquid separation membrane, into counterflow contact

with ammonia-containing wastewater, thereby recovering ammonia as an ammonium-sulfate solution (see Patent Document 5, for example). This technique allows ammonia-containing wastewater having a pH adjusted to 10 or higher to flow outside the hollow fiber membrane, while allowing the counterflow of a sulfuric acid solution with a pH of 2 or lower to flow inside the hollow fiber membrane, thereby removing and recovering ammonia within the wastewater. Gasified ammonia comes into contact with sulfuric acid flowing inside the hollow fiber membrane, and is recovered as ammonium sulfate.

[0008]

Methods using a vapor-liquid separation membrane can treat ammonia-containing wastewater economically with simple equipment to produce reusable ammonia as ammonium-sulfate solution. These methods, however, are disadvantageous in that further concentration of the ammonium-sulfate solution is necessary for reuse or recovery as a valuable commodity when the concentration of the ammonium sulfate in the ammonium-sulfate solution is low. In particular, ammonium-sulfate solution with a concentration of less than 25 percent by mass cannot be dealt with as a valuable commodity and may be treated as waste. Therefore, such ammonium-sulfate solution needs to be further concentrated by a reverse osmosis membrane (RO membrane) process, an ion exchange resin process, and other treatment processes.

## CITATION LIST

### PATENT LITERATURE

[0009]

Patent Document 1: JP 3987896 B

Patent Document 2: JP 2011-153043 A

Patent Document 3: JP 3272859 B

Patent Document 4: JP 3240694 B

Patent Document 5: JP 2013-202475 A

## SUMMARY

### TECHNICAL PROBLEM

[0010]

5           An object of one or more of embodiments of the present is to obtain an ammonium-sulfate solution having a high concentration of 25 percent by mass or higher, for example, in treatment of ammonia-containing wastewater for removing ammonia from the ammonia-containing wastewater using a vapor-liquid separation membrane and bringing a sulfuric acid solution into contact with the removed ammonia for recovery as an  
10 ammonium-sulfate solution.

### SOLUTION TO PROBLEM

[0011]

          In accordance with one aspect of the invention, an ammonia-containing wastewater treatment apparatus includes an ammonia removal unit having a vapor-liquid  
15 separation membrane, a first liquid chamber disposed adjacent to a first surface of the vapor-liquid separation membrane, and a second liquid chamber disposed adjacent to a second surface of the vapor-liquid separation membrane; an inlet-side valve configured to open and close a sulfuric acid solution inlet side of the second liquid chamber, and an outlet-side valve configured to open and close a sulfuric acid solution outlet side of the  
20 second liquid chamber; and a controller configured to close the inlet-side valve and the outlet-side valve when a flow of the sulfuric acid solution through the second liquid chamber is stopped. The ammonia removal unit removes ammonia from ammonia-containing wastewater flowing through the first liquid chamber and brings a sulfuric acid solution into contact with the ammonia which is removed, the sulfuric acid  
25 solution flowing through the second liquid chamber in counterflow with respect to the ammonia-containing wastewater, thereby recovering the ammonia as an ammonium sulfate solution.

[0012]

Preferably, the ammonia-containing wastewater treatment apparatus further includes a pressure relief unit configured to remove a pressure between the inlet-side valve and the outlet-side valve, and the controller is configured to close the inlet-side valve and the outlet-side valve and to actuate the pressure relief unit when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[0013]

Preferably, the ammonia-containing wastewater treatment apparatus includes a treated water circulation unit configured to circulate treated water obtained from the ammonia removal unit from an outlet side to an inlet side of the first liquid chamber, when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[0014]

Preferably, the ammonia-containing wastewater treatment apparatus includes a sulfuric acid adding unit configured to regulate a concentration of sulfuric acid in the sulfuric acid solution to be supplied to the second liquid chamber, the concentration of the sulfuric acid in the sulfuric acid solution to be added from the sulfuric acid adding unit being 50 percent by mass or greater.

[0015]

Preferably, the ammonia-containing wastewater treatment apparatus includes an ammonium-sulfate solution circulation unit configured to circulate the ammonium-sulfate solution which is recovered from an outlet side to an inlet side of the second liquid chamber; and an ammonium sulfate concentration measuring unit configured to measure a concentration of ammonium sulfate in the ammonium-sulfate solution which is recovered, the ammonium-sulfate solution which is recovered being extracted when the concentration of the ammonium sulfate which is measured is equal to or greater than a predetermined value.

[0016]

Preferably, in the ammonia-containing wastewater treatment apparatus, the ammonia-containing wastewater in the ammonia removal unit has a temperature in a range of 30 to 55°C.

[0017]

5 Preferably, in the ammonia-containing wastewater treatment apparatus, the ammonia-containing wastewater in the ammonia removal unit has a pH of 11 or greater.

[0018]

Preferably, the ammonia-containing wastewater treatment apparatus further includes an oxidizing agent removal unit configured to remove an oxidizing agent  
10 contained in the ammonia-containing wastewater before the ammonia-containing wastewater flows through the first liquid chamber.

[0019]

In accordance with another aspect of the invention, a method of treating ammonia-containing wastewater includes an ammonia removing step of removing  
15 ammonia from ammonia-containing wastewater flowing through a first liquid chamber in an ammonia removal unit comprising a vapor-liquid separation membrane, the first liquid chamber disposed adjacent to a first surface of the vapor-liquid separation membrane, and a second liquid chamber disposed adjacent to a second surface of the vapor-liquid separation membrane, and bringing a sulfuric acid solution into contact with the ammonia  
20 which is removed, the sulfuric acid solution flowing through the second liquid chamber in counterflow with respect to the ammonia-containing wastewater, thereby recovering the ammonia as an ammonium sulfate solution. An inlet-side valve configured to open and close a sulfuric acid solution inlet side of the second liquid chamber and an outlet-side valve configured to open and close a sulfuric acid solution outlet side of the second liquid  
25 chamber are closed when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[0020]

Preferably, in the ammonia-containing wastewater treating method, when the flow of the sulfuric acid solution through the second liquid chamber is stopped, the inlet-side valve configured to open and close the sulfuric acid solution inlet side of the second liquid chamber and the outlet-side valve configured to open and close the sulfuric acid solution outlet side of the second liquid chamber are closed, and a pressure relief unit configured to remove a pressure between the inlet-side valve and the outlet-side valve is actuated.

[0021]

Preferably, the ammonia-containing wastewater treating method includes a treated water circulating step of circulating treated water obtained by the ammonia removing step from an outlet side to an inlet side of the first liquid chamber, when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[0022]

Preferably, in the ammonia-containing wastewater treating method, the concentration of the sulfuric acid in the sulfuric acid solution to be added for regulating the concentration of the sulfuric acid in the sulfuric acid solution to be supplied to the second liquid chamber is 50 percent by mass or greater.

[0023]

Preferably, in the ammonia-containing wastewater treating method, the ammonium-sulfate solution which is recovered is circulated from an outlet side to an inlet side of the second liquid chamber, a concentration of ammonium sulfate in the ammonium-sulfate solution which is recovered is measured, and the ammonium-sulfate solution which is recovered is extracted when the concentration of the ammonium sulfate which is measured is equal to or greater than a predetermined value.

[0024]

Preferably, in the ammonia-containing wastewater treating method, the ammonia-containing wastewater in the ammonia removing step has a temperature in a range of 30 to 55°C.

[0025]

Preferably, in the ammonia-containing wastewater treating method, the ammonia-containing wastewater in the ammonia removing step has a pH of 11 or greater.  
[0026]

Preferably, the ammonia-containing wastewater treating method further includes  
5 an oxidizing agent removing step of removing an oxidizing agent contained in the ammonia-containing wastewater before the ammonia-containing wastewater flows through the first liquid chamber.

#### ADVANTAGEOUS EFFECTS OF INVENTION

10 [0027]

According to the present invention, in the process of removing ammonia from ammonia-containing wastewater using a vapor-liquid separation membrane and bringing a sulfuric acid solution into contact with the removed ammonia to recover the ammonia as an ammonium sulfate solution, a highly concentrated ammonium sulfate solution with 25  
15 percent by mass or higher, for example, can be obtained.

#### BRIEF DESCRIPTION OF DRAWINGS

[0028]

[FIG. 1]

20 FIG. 1 is a diagram schematically illustrating the structure of an example ammonia-containing wastewater treatment apparatus according to an embodiment of the present invention.

[FIG. 2]

FIG. 2 is a diagram schematically illustrating the structure of another example  
25 ammonia-containing wastewater treatment apparatus according to an embodiment of the present invention.

#### DESCRIPTION OF EMBODIMENTS

[0029]

Embodiments of the present invention will be described. The present embodiments are only examples for implementing the present invention, and the present invention is not limited to these embodiments.

5 [0030]

FIG. 1 schematically illustrates an example ammonia-containing wastewater treatment apparatus according to an embodiment of the present invention, the structure of which will be described. An ammonia-containing wastewater treatment apparatus 1 includes an ammonia removal device 16 serving as an ammonia removing unit, and a  
10 circulation tank 18 serving as an ammonium-sulfate solution circulator. The ammonia-containing wastewater treatment apparatus 1 may further include a raw water tank 10, a heat exchanger 12 serving as a heater, a pH adjusting tank 14, a sulfuric acid storage tank 20 serving as a sulfuric acid adding unit, and a pH adjustor storage tank 22.

[0031]

15 The ammonia removal device 16 includes a vapor-liquid separation membrane 26, and a first liquid chamber 24a and a second liquid chamber 24b defined by the vapor-liquid separation membrane 26. The vapor-liquid separation membrane 26 is a hollow fiber membrane, for example, which does not allow passage of liquid but allows passage of gaseous ammonia. The first liquid chamber 24a is disposed adjacent to a first surface of  
20 the vapor-liquid separation membrane 26 and the second liquid chamber 24b is disposed adjacent to a second surface of the vapor-liquid separation membrane 26.

Ammonia-containing wastewater is supplied to the first liquid chamber 24a and a sulfuric acid solution is supplied to the second liquid chamber 24b.

[0032]

25 In the ammonia-containing wastewater treatment apparatus 1 illustrated in FIG. 1, a raw water pipe 30 is connected to a raw water inlet of the raw water tank 10. An outlet of the raw water tank 10 and a raw water inlet of the heat exchanger 12 are connected to each other by a raw water supply pipe 32, and a raw water outlet of the heat exchanger 12

and an inlet of the pH adjusting tank 14 are connected to each by a raw water supply pipe 34. An outlet of the pH adjusting tank 14 and an inlet of the first liquid chamber 24a disposed at a first end of the ammonia removal device 16 are connected by a pH-adjusted water pipe 36. An outlet of the first liquid chamber 24a disposed at a second end of the ammonia removal device 16 and a treated water inlet of the heat exchanger 12 are connected by a treated water circulation pipe 38, and a treated water outlet of the heat exchanger 12 and a treated water inlet of the raw water tank 10 are connected by a treated water circulation pipe 40 via a valve 62. Between the treated water outlet of the heat exchanger 12 and the valve 62, a treated water discharge pipe 54 is connected via a treated water extraction valve 64. An outlet of the circulation tank 18 and an inlet of the second liquid chamber 24b disposed at the second end of the ammonia removal device 16 are connected by an ammonium-sulfate solution circulation pipe 42 via an inlet-side valve 56, and an outlet of the second liquid chamber 24b and an inlet of the circulation tank 18 disposed at the first end of the ammonia removal device 16 are connected by an ammonium-sulfate solution circulation pipe 44 via an outlet-side valve 58. A recovered ammonium-sulfate solution pipe 50 is connected to an extraction port of the circulation tank 18. An outlet of the sulfuric acid storage tank 20 is connected to the circulation tank 18 by a sulfuric acid pipe 46. An outlet of the pH adjustor storage tank 22 is connected to the pH adjusting tank 14 by a pH adjustor pipe 48. An ammonium sulfate concentration measuring device 66 may be mounted to the circulation tank 18.

[0033]

An ammonia-containing wastewater treatment method according to the present embodiment and the operation of the ammonia-containing wastewater treatment apparatus 1 will be described.

[0034]

The ammonia-containing wastewater, which is raw water, is stored in the raw water tank 10, as required, through the raw water pipe 30, and is thereafter routed to the heat exchanger 12, as required, through the raw water supply pipe 32. The

ammonia-containing wastewater, which is raw water, undergoes heat exchange, as required, with treated water supplied through the treated water pipe 38, and is heated in the heat exchanger 12 (heating process). If the temperature of the ammonia-containing wastewater is a predetermined value, the heating process need not be performed.

5 [0035]

The ammonia-containing wastewater which has been heated as required in the heat exchanger 12 is routed through the raw water supply pipe 34 to the pH adjusting tank 14 as required. In the pH adjusting tank 14, a pH adjustor is supplied from the pH adjustor storage tank 22 through the pH adjustor pipe 48 as required, to adjust the pH of the ammonia-containing wastewater to a predetermined value (pH adjusting process). The pH adjustor used in the pH adjusting process is, for example, alkali such as sodium hydroxide solution or acid such as hydrochloric acid. During the pH adjusting process, the ammonia-containing wastewater is preferably adjusted to pH 11 or greater to increase the ammonia removal rate in the ammonia removing process, which will be described

10 below, by dissociating ammonium ions in the ammonia-containing wastewater to form ammonia gas. In consideration of influences on the membrane and the pipe materials, for example, the ammonia-containing wastewater is more preferably adjusted to a range from pH 11 to pH 12. If the pH of the ammonia-containing wastewater is the predetermined value, the pH adjusting process need not be performed.

20 [0036]

The pH-adjusted water having undergone pH adjustment as required is routed through the pH-adjusted water pipe 36 from the inlet disposed at the first end of the ammonia removal device 16 to the first liquid chamber 24a. In the ammonia removal device 16, the vapor-liquid separation membrane 26 which inhibits passage of liquid and

25 allows passage of ammonia is used to remove ammonia from the ammonia-containing wastewater. The treated water from which ammonia has been removed is routed from the outlet of the first liquid chamber 24a disposed at the second end of the ammonia removal device 16 through the treated water pipe 38 to the heat exchanger 12. On the other hand,

with the inlet-side valve 56 and the outlet-side valve 58 being opened, the sulfuric acid solution, supplied from the sulfuric acid storage tank 20 through the sulfuric acid pipe 46 and stored in the circulation tank 18, is supplied through the ammonium-sulfate solution circulation pipe 42 from the inlet disposed at the second end of the ammonia removal device 16 to the second liquid chamber 24b. In the second liquid chamber 24b, the sulfuric acid solution is caused to flow in a counterflow with respect to the ammonia-containing wastewater in the first liquid chamber 24a. For example, the ammonia-containing wastewater is caused to flow outside the hollow fiber membrane (first liquid chamber 24a) and the sulfuric acid solution is caused to flow inside the hollow fiber membrane (second liquid chamber 24b). The ammonia passing through the vapor-liquid separation membrane 26 comes into contact with the sulfuric acid solution flowing in the second liquid chamber 24b of the ammonia removal device 16 to produce ammonium sulfate (ammonia removing process).

[0037]

The treated water transported to the heat exchanger 12 undergoes heat exchange in the heat exchanger 12 with the ammonia-containing wastewater routed thereto through the raw water supply pipe 32 and is cooled (cooling process), as required. The cooled treated water is discharged through the treated water discharge pipe 54, with the valve 62 being closed and the valve 64 being opened.

[0038]

The ammonium sulfate produced in the second liquid chamber 24b of the ammonia removal device 16 is routed, in a state dissolved in the sulfuric acid solution, from the outlet of the second liquid chamber 24b disposed at the first end of the ammonia removal device 16 through the ammonium-sulfate solution circulation pipe 44 to the circulation tank 18. The sulfuric acid solution is circulated through the circulation tank 18 and the ammonium-sulfate solution circulation pipes 42 and 44 until the concentration of the ammonium sulfate reaches the predetermined value (ammonium-sulfate solution circulating process). At this time, the sulfuric acid solution is supplied from the sulfuric

acid storage tank 20 through the sulfuric acid pipe 46 to the circulation tank 18, to adjust the pH of the circulating sulfuric acid solution to the predetermined value. Once the concentration of the ammonium sulfate in the circulating sulfuric acid solution which is recovered reaches the predetermined value or greater, the ammonium sulfate is discharged  
5 from the circulation tank 18 through the recovered ammonium-sulfate solution pipe 50, as a recovered ammonium-sulfate solution.

[0039]

The present inventors have carried out studies and found that, in treating ammonia-containing wastewater using a vapor-liquid separation membrane, not only  
10 ammonia gas but also water vapor moves through the vapor-liquid separation membrane. This water vapor may dilute the recovered ammonium-sulfate solution, lowering the concentration of the ammonium sulfate in the ammonium-sulfate solution to a level below the predetermined value, which is lower than an expected value. It is particularly clear that, in treating ammonia-containing wastewater having a relatively low concentration,  
15 such as about 3,000 mg/L or less, for example, such a movement of the water vapor cannot be disregarded in order to obtain ammonium-sulfate solution of 25 percent by mass or greater.

[0040]

The present inventors have further studied the movement of the water vapor  
20 through a vapor-liquid separation membrane and revealed that even during interruption of the flow of the ammonia-containing wastewater through the vapor-liquid separation membrane, the water vapor moves through the vapor-liquid separation membrane and lowers the concentration of the ammonium-sulfate solution. Specifically, in the apparatus illustrated in FIG. 1, when the flow of the ammonia-containing wastewater through the  
25 vapor-liquid separation membrane 26 was stopped and this state was maintained for about a half day, or when the water level of the raw water tank 10 was lowered and the flow of the ammonia-containing wastewater was stopped, for example, water vapor passed through the vapor-liquid separation membrane 26 and continuously raised the water level of the

ammonium-sulfate solution in the circulation tank 18 storing the ammonium-sulfate solution, to thereby lower the concentration of the ammonium sulfate.

[0041]

The present inventors have therefore disposed the inlet-side valve 56 and the outlet-side valve 58 on the inlet side and the outlet side, respectively, of the sulfuric acid solution which flows through the downstream side of the vapor-liquid separation membrane 26, that is, the second liquid chamber 24b, in an apparatus that removes ammonia from ammonia-containing wastewater using a vapor-liquid separation membrane to recover ammonium-sulfate solution. The inventors then found that, by placing both the inlet-side valve 56 and the outlet-side valve 58 in a closed state when the flow of the sulfuric acid solution through the second liquid chamber 24b is stopped, the movement of the water vapor to the circulation tank 18 through the ammonium-sulfate solution circulation pipes 42 and 44 is regulated, even if the water vapor moves through the vapor-liquid separation membrane 26. Consequently a highly concentrated ammonium-sulfate solution, such as 25 percent by mass or greater, can be obtained. The inlet-side valve 56 and the outlet-side valve 58 may be opened or closed by a controller which is not shown. When the water level of the raw water tank 10 is low or the water level of the circulation tank 18 is high, a "standby" state may be set. That is, the flow of the sulfuric acid solution through the second liquid chamber 24b may be stopped and both the inlet-side valve 56 and the outlet-side valve 58 may be closed, to prevent the water vapor from flowing into the ammonium-sulfate solution and thus reducing the concentration of the ammonium-sulfate solution.

[0042]

Preferably, the ammonia-containing wastewater treatment apparatus 1 is placed in the "standby" state, and the sulfuric acid solution accumulated in the second liquid chamber 24b is blown off before restarting the operation. This also regulates the reduction in the concentration of the ammonium-sulfate solution recovered after restart of the operation.

[0043]

Studies by the present inventors have also revealed that even when the inlet-side valve 56 and the outlet-side valve 58 are closed, with the flow of the sulfuric acid solution through the second liquid chamber 24b being stopped, the concentration of the ammonium-sulfate solution remaining downstream of the vapor-liquid separation membrane 26, that is, in the second liquid chamber 24b, for example, decreases significantly and the pressure between the inlet-side valve 56 and the outlet-side valve 58 increases by about 0.05 to 0.4 MPa after several days. Therefore, as in an ammonia-containing wastewater treatment apparatus 3 illustrated in FIG. 2, a pressure relief valve 60 serving as a pressure relief unit that relieves the pressure between the inlet-side valve 56 and the outlet-side valve 58 is connected between the inlet-side valve 56 and inlet of the second liquid chamber 24b via a pressure relief pipe 52, for example. The apparatus is then controlled to close the inlet-side valve 56 and the outlet-side valve 58 and open the pressure relief valve 60 when the flow of the sulfuric acid solution through the second liquid chamber 24b is stopped. This structure can regulate a pressure rise on the downstream side of the vapor-liquid separation membrane 26 to thereby prevent overpressure from being applied to the vapor-liquid separation membrane 26 even when the operation is interrupted for a long time period. The pressure relief pipe 52 and the pressure relief valve 60 may be disposed between the outlet of the second liquid chamber 24b and the outlet-side valve 58. The inlet-side valve 56, the outlet-side valve 58, and the pressure relief valve 60 may be opened or closed by a controller which is not shown.

[0044]

When the flow of the sulfuric acid solution through the second liquid chamber 24b is stopped, with the valve 62 being open and the valve 64 being closed, the treated water may be circulated from the outlet side of the first liquid chamber 24a, through the treated water circulation pipes 38 and 40 and the raw water tank 10 serving as a treated water circulation unit, to the inlet side of the first liquid chamber 24a (treated water circulating process). The operation to circulate the treated water from the upstream side of the

vapor-liquid separation membrane 26, that is, from the first liquid chamber 24a, to the raw water tank 10 allows the temperature of the ammonia-containing wastewater, which is raw water, to be maintained within a predetermined range by warming or heating the ammonia-containing wastewater, so that the processing after restart of the operation can be stabilized.

[0045]

The ammonia-containing wastewater to be treated includes, for example, ammonia-containing wastewater discharged from electronic industry plants, such as semiconductor plants, chemical plants, thermal power plants, and other plants.

[0046]

When the ammonia-containing wastewater contains an oxidizing agent such as hydrogen peroxide, as in the ammonia-containing wastewater discharged from an electronic industry plant such as a semiconductor plant, the oxidizing agent may be removed by an active carbon treatment apparatus, for example, serving as an oxidizing agent removal unit, before the ammonia removal device 16 (oxidizing agent removing process). This process can prevent a decrease in the ammonia removal rate during the ammonia removing process and deterioration of the vapor-liquid separation membrane caused by the oxidizing agent such as hydrogen peroxide.

[0047]

The concentration of ammonia in the ammonia-containing wastewater which is raw water is not particularly limited. Preferably, to obtain the recovered ammonium-sulfate solution with the ammonium sulfate concentration being adjusted to 25 percent by mass or higher, and also to prevent precipitation of the ammonium sulfate, the concentration of ammonia in the ammonia-containing wastewater is preferably controlled to between 900 mg/L and 2,200 mg/L.

[0048]

When the concentration of ammonia in the ammonia-containing wastewater is low (e.g., less than 900 mg/L), the ammonia may be concentrated by a reverse osmosis

membrane treatment, for example, upstream of the ammonia removal device 16. Further, to concentrate the ammonium sulfate, an ammonium-sulfate solution produced by treating low-concentration ammonia-containing wastewater is returned from the circulation tank 18 to the raw water tank 10, for example, for further ammonia treatment.

5 [0049]

Preferably, a heater such as the heat exchanger 12 is used to heat the raw water to a range between 30 and 55°C and preferably between 35 and 55°C and route the ammonia-containing wastewater to the ammonia removal device 16. When the temperature of the raw water is less than 30°C the ammonia in the ammonia-containing wastewater is difficult to gasify, lowering the ammonia removal rate in the ammonia removal device 16. In place of the heat exchanger 12, a device capable of warming, such as a heater, may be disposed on at least one of the raw water tank 10, the raw water pipe 30, and the raw water supply pipe 32, in order to heat the raw water.

[0050]

15 During the ammonia removing process, the pH of ammonia-containing wastewater to be treated is preferably 11 or greater in terms of the ammonia removing rate. If the pH of the ammonia-containing wastewater to be treated is below 11, the ammonia in the ammonia-containing wastewater is difficult to gasify, thereby lowering the ammonia removing rate.

20 [0051]

The vapor-liquid separation membrane 26 is not particularly limited so long as it does not allow passage of a liquid and allows passage of gaseous ammonia. The vapor-liquid separation membrane 26 is a hydrophobic porous hollow fiber membrane, for example. A hollow fiber membrane with the diameter of hollow fiber being about 300 μm, the hollow size being about 0.03 μm, and the (average) porosity being about 40 to about 50%, for example, may be used. Gaseous ammonia contained in the ammonia-containing wastewater passes through the vapor-liquid separation membrane 26 having the above structure and is removed from the ammonia-containing wastewater.

[0052]

The sulfuric acid solution is preferably introduced from the sulfuric acid storage tank 20 such that the pH of the circulating sulfuric acid solution is maintained at 2 or less, for example, in a range of 1 to 2, and preferably in a range of 1.5 to 2. The pH of the circulating sulfuric acid solution, which is 2 or greater, may lower the ammonia removing rate.

[0053]

The sulfuric acid solution to be added from the sulfuric acid storage tank 20 preferably has as high a concentration as possible. In terms of handling, the concentration of the sulfuric acid in the sulfuric acid solution to be added from the sulfuric acid storage tank 20 is preferably 50 percent by mass or greater.

[0054]

As described above, when the concentration of the recovered ammonium sulfate in the circulating sulfuric acid solution reaches a predetermined value or greater, such as 25 percent by mass or greater, for example, the recovered ammonium sulfate is discharged from the circulation tank 18 through the ammonium-sulfate solution pipe 50 as a recovered ammonium-sulfate solution.

[0055]

The concentration of the ammonium sulfate in the circulating sulfuric acid solution may be measured using an ammonium sulfate concentration measuring device 66 serving as an ammonium sulfate concentration measuring unit such as a hydrometer and a concentration meter. When the concentration of the ammonium sulfate which is measured reaches the predetermined concentration or greater, such as 25 percent by mass or higher (e.g., when the measurement value of the hydrometer indicates a specific gravity of about 1.14 or greater of the 25 percent by mass ammonium-sulfate solution), the ammonium sulfate may be automatically collected as the recovered ammonium-sulfate solution from the circulation tank 18 through the ammonium-sulfate solution pipe 50. While, in the examples illustrated in FIGs. 1 and 2, the ammonium sulfate concentration

measuring device 66 is disposed in the circulation tank 18, the ammonium sulfate concentration measuring device 66 may be disposed in the ammonium-sulfate solution circulation pipe 42. Also, to obtain the concentration at which ammonium sulfate would not easily precipitate (e.g., 40 percent by mass or less), a device which, based on the measured concentration of ammonium sulfate, automatically supplies water for dilution may be further provided.

[0056]

When the vapor-liquid separation membrane 26 is contaminated by metallic salts, for example, and the ammonia removing rate is reduced, or to prevent a reduction in the ammonia removing rate, acid cleaning may be applied to the vapor-liquid separation membrane 26 at a predetermined time (acid cleaning process). For example, an acid storage tank is further disposed to supply an acid solution through the pH-adjusted water pipe 36 to the first liquid chamber 24a of the ammonia removal device 16 for cleaning the vapor-liquid separation membrane 26. Alternatively, the sulfuric acid solution from the sulfuric acid storage tank 20 may be partially supplied to the first liquid chamber 24a.

[0057]

An acid solution such as sulfuric acid, hydrochloric acid, and citric acid can be used in the acid cleaning process.

[0058]

The present invention will be more specifically described hereinafter using an example and a comparative example. However, the present invention is not limited to the following examples.

[0059]

Ammonia-containing wastewater was treated under the following test conditions.

[Test Conditions]

- Vapor-liquid separation membrane used :polypropylene porous hollow fiber membrane module
- Area of membrane: :1.4 m<sup>2</sup>

- Amount of water: 0.0145 m<sup>3</sup>/h
- Water temperature :30°C
- Ammonia-containing wastewater pH: 12 or greater
- Acid-side pH:2 or less

5 [0060]

Ammonia-containing wastewater having an ammonia concentration of 1796 mg/L was caused to flow through the upstream side (first liquid chamber) of a vapor-liquid separation membrane for 6 hours. The flow rates on the upstream side (first liquid chamber) and the downstream side (second liquid chamber) were set to 14.5 L/h, and 19.0 L/h, respectively. The ammonia-containing wastewater which flows through the first liquid chamber was made to have a pH of 12 or greater by adding a sodium hydroxide solution thereto, and the pH of the solution which flows through the second liquid chamber was maintained at 2 or less by adding 50 percent by mass of sulfuric acid solution to the initial 14 percent by mass of ammonium-sulfate solution.

15 [0061]

#### EXAMPLE 1

After the ammonia-containing wastewater was allowed to flow for 6 hours for treatment, the flow of the ammonia-containing wastewater and the flow of the sulfuric acid solution were stopped for 17 hours, and the inlet-side valve for opening or closing the inlet side of the sulfuric acid solution and the outlet-side valve for opening or closing the outlet side were controlled to be closed.

[0062]

#### COMPARISON EXAMPLE 1

After the ammonia-containing wastewater was allowed to flow for 6 hours for treatment, the flow of the ammonia-containing wastewater and the flow of the sulfuric acid solution were stopped for 17 hours, and both the inlet-side valve and the outlet-side valve were opened.

[0063]

(Result of Experiment)

Results of the experiments are shown in Table 1.

[0064]

[Table 1]

|                                    | raw water | Example 1 | Comparative<br>Example 1 |
|------------------------------------|-----------|-----------|--------------------------|
| $\text{NH}_4^+$ [mg/L]             | 1,796     | 403       | 403                      |
| ammonium sulfate [percent by mass] | 14.4      | 29.7      | 22.5                     |

5

[0065]

In Example 1, the ammonium-sulfate solution could be stably recovered at the concentration of 25 percent by mass or greater; whereas in Comparative Example 1, the concentration of the final ammonium-sulfate solution was below 25 percent by mass (22.5 percent by mass). It is considered that, in Comparative Example 1, because both the inlet-side valve and the outlet-side valve were opened during the 17-hour interruption, water vapor was transmitted through the vapor-liquid separation membrane to dilute the ammonium-sulfate solution within the circulation tank, thereby lowering the concentration of the ammonium sulfate.

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15

#### REFERENCE SIGNS LIST

[0066]

1, 3 ammonia-containing wastewater treatment apparatus, 10 raw water tank, 12 heat exchanger, 14 pH adjusting tank, 16 ammonia removal device, 18 circulation tank, 20 sulfuric acid storage tank, 22 pH adjustor storage tank , 24a first liquid chamber, 24b second liquid chamber, 26 vapor-liquid separation membrane, 30 raw water pipe, 32, 34 raw water supply pipe, 36 pH-adjusted water pipe, 38, 40 treated water circulation pipe, 42, 44 ammonium-sulfate solution circulation pipe, 46 sulfuric acid pipe, 48 pH adjustor pipe, 50 recovered ammonium-sulfate solution pipe, 52 pressure relief pipe, 54 treated water

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discharge pipe, 56 inlet-side valve, 58 outlet-side valve, 60 pressure relief valve, 62 valve, 64 treated water extraction valve, 66 ammonium sulfate concentration measuring device.

## CLAIMS

### [Claim 1]

- 5           An ammonia-containing wastewater treatment apparatus, comprising:
- an ammonia removal unit comprising a vapor-liquid separation membrane, a first liquid chamber disposed adjacent to a first surface of the vapor-liquid separation membrane, and a second liquid chamber disposed adjacent to a second surface of the vapor-liquid separation membrane, the ammonia removal unit removing ammonia from
- 10   ammonia-containing wastewater flowing through the first liquid chamber and bringing a sulfuric acid solution into contact with the ammonia which is removed, the sulfuric acid solution flowing through the second liquid chamber in counterflow with respect to the ammonia-containing wastewater, thereby recovering the ammonia as an ammonium sulfate solution;
- 15           an inlet-side valve configured to open and close a sulfuric acid solution inlet side of the second liquid chamber, and an outlet-side valve configured to open and close a sulfuric acid solution outlet side of the second liquid chamber; and
- a controller configured to close the inlet-side valve and the outlet-side valve when a flow of the sulfuric acid solution through the second liquid chamber is stopped.

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### [Claim 2]

- The ammonia-containing wastewater treatment apparatus according to claim 1, further comprising:
- a pressure relief unit configured to remove a pressure between the inlet-side valve
- 25   and the outlet-side valve,
- wherein the controller is configured to close the inlet-side valve and the outlet-side valve and to actuate the pressure relief unit when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[Claim 3]

The ammonia-containing wastewater treatment apparatus according to claims 1 or 2, comprising:

- 5           a treated water circulation unit configured to circulate treated water obtained from the ammonia removal unit from an outlet side to an inlet side of the first liquid chamber, when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[Claim 4]

- 10           The ammonia-containing wastewater treatment apparatus according to any one of claims 1 to 3, comprising:

          a sulfuric acid adding unit configured to regulate a concentration of sulfuric acid in the sulfuric acid solution to be supplied to the second liquid chamber, wherein

- the concentration of the sulfuric acid in the sulfuric acid solution to be added from  
15   the sulfuric acid adding unit is 50 percent by mass or greater.

[Claim 5]

The ammonia-containing wastewater treatment apparatus according to any one of claims 1 to 4, comprising:

- 20           an ammonium-sulfate solution circulation unit configured to circulate the ammonium-sulfate solution which is recovered from an outlet side to an inlet side of the second liquid chamber; and

          an ammonium sulfate concentration measuring unit configured to measure a concentration of ammonium sulfate in the ammonium-sulfate solution which is recovered,

- 25   wherein

          the ammonium-sulfate solution which is recovered is extracted when the concentration of the ammonium sulfate which is measured is equal to or greater than a predetermined value.

[Claim 6]

The ammonia-containing wastewater treatment apparatus according to any one of claims 1 to 5, wherein

5           the ammonia-containing wastewater in the ammonia removal unit has a temperature in a range of 30 to 55°C.

[Claim 7]

10           The ammonia-containing wastewater treatment apparatus according to any one of claims 1 to 6, wherein

            the ammonia-containing wastewater in the ammonia removal unit has a pH of 11 or greater.

[Claim 8]

15           The ammonia-containing wastewater treatment apparatus according to claim 1 to 7, further comprising:

            an oxidizing agent removal unit configured to remove an oxidizing agent contained in the ammonia-containing wastewater before the ammonia-containing wastewater flows through the first liquid chamber.

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[Claim 9]

            A method of treating ammonia-containing wastewater comprising:

            an ammonia removing step of removing ammonia from ammonia-containing wastewater flowing through a first liquid chamber in an ammonia removal unit comprising  
25   a vapor-liquid separation membrane, the first liquid chamber disposed adjacent to a first surface of the vapor-liquid separation membrane, and a second liquid chamber disposed adjacent to a second surface of the vapor-liquid separation membrane, and bringing a sulfuric acid solution into contact with the ammonia which is removed, the sulfuric acid

solution flowing through the second liquid chamber in counterflow with respect to the ammonia-containing wastewater, thereby recovering the ammonia as an ammonium sulfate solution,

5 wherein an inlet-side valve configured to open and close a sulfuric acid solution inlet side of the second liquid chamber, and an outlet-side valve configured to open and close a sulfuric acid solution outlet side of the second liquid chamber, are closed when the flow of the sulfuric acid solution through the second liquid chamber is stopped.

[Claim 10]

10 The method of treating ammonia-containing wastewater according to claim 9, wherein,

when the flow of the sulfuric acid solution through the second liquid chamber is stopped, the inlet-side valve configured to open and close the sulfuric acid solution inlet side of the second liquid chamber, and the outlet-side valve configured to open and close  
15 the sulfuric acid solution outlet side of the second liquid chamber, are closed, and a pressure relief unit configured to remove a pressure between the inlet-side valve and the outlet-side valve is actuated.