

SYSTEM AND METHOD FOR RECOVERY OF AMMONIA FROM AN AQUEOUS SOLUTION

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Application Serial No. 63/451,069 titled “System and Method of Using Gas Permeable Membrane Contactors for the Removal of Ammonia from Wastewater” filed March 9, 2023, which is incorporated herein by reference in its entirety for all purposes.

10 FIELD OF TECHNOLOGY

Aspects and embodiments disclosed herein are generally related to systems and methods for recovery of ammonia, and more specifically, to systems and methods using gas permeable membrane contactors for recovery of ammonia from wastewater.

15 SUMMARY

In accordance with one aspect, there is provided a system for recovering ammonia from an aqueous solution. The system may comprise a plurality of modules arranged in series, each module comprising a plurality of membranes, each membrane having a lumen side and a shell side. The plurality of modules may comprise a lead module having a shell inlet fluidly connected to a source of the aqueous solution comprising ammonia, a shell outlet, a lumen inlet, and a lumen outlet. The plurality of modules may comprise an end module having a lumen inlet fluidly connected to a source of an acidic solution, a lumen outlet, a shell inlet, and a shell outlet. The shell outlet of the lead module may be fluidly connected to the shell inlet of the end module, and the lumen outlet of the end module may be fluidly connected to the lumen inlet of the lead module.

In some embodiments, the system further comprises at least one intermediate module having a shell inlet, a shell outlet, a lumen inlet, and a lumen outlet, the shell inlet of the intermediate module being fluidly connected to the shell outlet of the lead module, the shell outlet of the intermediate module being fluidly connected to the shell inlet of the end module, the lumen inlet of the intermediate module being fluidly connected to the lumen outlet of the end module, and the lumen outlet of the intermediate module fluidly connected to the lumen inlet of the lead module.

In some embodiments, the aqueous solution is substantially homogeneous.

In some embodiments, the system may comprise a temperature control subsystem configured to control temperature of the aqueous solution.

In some embodiments, the system may comprise at least one sensor configured to measure at least one property of the aqueous solution selected from temperature, pH,
5 ammonia concentration, or concentration of a contaminant.

In some embodiments, the lumen outlet of the lead module is fluidly connected to a reservoir comprising the source of the acidic solution by a return conduit.

In some embodiments, the reservoir comprises an inlet fluidly connectable to a source of an acid and a discharge outlet.

10 In some embodiments, the system may comprise at least one sensor configured to measure at least one property of the acidic solution selected from temperature, pH, density, specific gravity, conductivity, ammonia concentration, concentration of the acid, or ionic concentration.

In some embodiments, the system may comprise a pH control subsystem configured
15 to control pH of the acidic solution.

In some embodiments, the system may comprise a flow control subsystem configured to control flow rate of the aqueous solution.

In some embodiments, the system may comprise a flow control subsystem configured to control flow rate of the acidic solution.

20 In some embodiments, the plurality of membranes are hydrophobic and the module is operable at a temperature of 120°F – 150°F.

In accordance with another aspect, there is provided a system for recovering ammonia from an aqueous solution. The system may comprise a plurality of rows arranged in parallel, each row comprising a plurality of modules arranged in series, each module comprising a
25 plurality of membranes, each membrane having a lumen side and a shell side. Each lead module of the row may have a shell inlet fluidly connected to a source of the aqueous solution comprising ammonia, a lumen inlet, a shell outlet, and a lumen outlet. Each end module of the row may have a lumen inlet fluidly connected to a source of an acidic solution, a lumen outlet fluidly connected to the lumen inlet of the corresponding lead module, a shell
30 inlet fluidly connected to the shell outlet of the corresponding lead module, and a shell outlet. The lumen outlet of each lead module may be fluidly connected to the source of the acidic solution by a return conduit.

In some embodiments, each row further comprises at least one intermediate module having a shell inlet, a shell outlet, a lumen inlet, and a lumen outlet, the shell inlet of the

intermediate module being fluidly connected to the shell outlet of the corresponding lead module, the shell outlet of the intermediate module being fluidly connected to the shell inlet of the corresponding end module, the lumen inlet of the intermediate module being fluidly connected to the lumen outlet of the corresponding end module, and the lumen outlet of the intermediate module being fluidly connected to the lumen inlet of the corresponding lead module.

In some embodiments, the system may comprise a pH control subsystem configured to control pH of the acidic solution.

In some embodiments, the system may comprise at least one flow control subsystem configured to control flow rate of the acidic solution and/or the source of the aqueous solution.

In some embodiments, the system may comprise a temperature control subsystem configured to control temperature of the aqueous solution.

In accordance with another aspect, there is provided a method of treating an aqueous solution comprising ammonia with a system comprising a plurality of modules, each module comprising a plurality of membranes, each membrane having a lumen side and a shell side. The method may comprise directing the aqueous solution comprising ammonia to a shell inlet of a lead module to produce a first effluent, the first effluent being fluidly connected to a shell inlet of an end module. The method may comprise directing an acidic solution to a lumen inlet of the end module, the ammonia being filtered through the plurality of membranes of the end module to produce a first intermediate product comprising ammonium and a second effluent. The first intermediate product may be fluidly connected to a lumen inlet of the lead module, the ammonia being filtered through the plurality of membranes of the lead module to produce a second intermediate product comprising ammonium.

In some embodiments, the method may comprise directing the second intermediate product to a reservoir comprising an acid to produce the acidic solution.

In some embodiments, the method may comprise controlling pH of the acidic solution by addition of an effective amount of the acid.

In some embodiments, the method may comprise withdrawing a product comprising ammonium from the reservoir.

In some embodiments, the method may comprise drying the product comprising ammonium to produce a fertilizer product.

In some embodiments, the method may comprise directing the second effluent to a point of use.

In some embodiments, the method may comprise controlling temperature of the aqueous solution to be between 95°F and 150°F.

In some embodiments, the method may comprise controlling flow rate of the aqueous solution and the acidic solution.

5 The disclosure contemplates all combinations of any one or more of the foregoing aspects and/or embodiments, as well as combinations with any one or more of the embodiments set forth in the detailed description and any examples.

BRIEF DESCRIPTION OF THE DRAWINGS

10 The accompanying drawings are not intended to be drawn to scale. In the drawings, each identical or nearly identical component that is illustrated in various figures is represented by a like numeral. For purposes of clarity, not every component may be labeled in every drawing. In the drawings:

FIG. 1 a box diagram of a system for removing ammonia from an aqueous solution,
15 according to one embodiment;

FIG. 2 is a box diagram of an alternate system for removing ammonia from an aqueous solution, according to one embodiment;

FIG. 3 is a box diagram of an alternate system for removing ammonia from an aqueous solution, according to one embodiment;

20 FIG. 4 is a box diagram of an alternate system for removing ammonia from an aqueous solution, according to one embodiment;

FIG. 5 is a schematic diagram of a system for removing ammonia from an aqueous solution, according to one embodiment;

FIG. 6 is a graph showing percent ammonia removal from an aqueous solution,
25 according to one embodiment;

FIG. 7 is a graph showing percent ammonia removal from an aqueous solution, according to one embodiment; and

FIG. 8 is a graph showing percent ammonia removal from an aqueous solution, according to one embodiment.

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DETAILED DESCRIPTION

The systems and methods disclosed herein may be employed to render aqueous solutions, for example, wastewaters, suitable for secondary use or discharge to the environment. In particular, the systems and methods disclosed herein may be employed to

reduce a concentration of nitrogen-containing compounds, such as ammonia, from aqueous solutions. In accordance with certain embodiments, the systems and methods disclosed herein may promote removal of nitrogen-containing compounds from aqueous solutions by gas transfer, such as with a gas permeable membrane contactor. The systems and methods
5 disclosed herein may promote recovery of nitrogen-containing compounds in an acidic solution.

Gas transfer generally involves contact of the aqueous solution with a membrane configured to enable gas-liquid separation by being permeable to gasses and impermeable to liquids. For instance, flowing an aqueous solution inside a gas transfer membrane may
10 selectively pass dissolved gasses, leaving substantially pure solvents on the filtrate side. The dissolved gas may be absorbed from a feed stream into an acid stream.

Gas permeable membrane contactors may be used to remove dissolved gases from compatible liquid streams without dispersion. The membranes may be configured to prevent redissolution of the gas into the liquid. A membrane contactor, also referred to as a “module”
15 herein, may be designed to contain a plurality of microporous hollow fibers placed inside a contactor housing. The hollow fibers may define a lumen side and a shell or housing side. The membranes may be arranged with substantially uniform spacing to allow for high flow capacity and utilization of the total membrane surface area. Unlike dispersed-phase contactors, such as packed columns, membrane contactors may provide a constant interfacial
20 area for transfer over the entire range of flow rates. Furthermore, utilizing a hydrophobic membrane may prevent aqueous liquids from penetrating the membrane pores.

One exemplary gas transfer membrane module is the Liqui-CelTM Membrane contactor (distributed by 3MTM, Maplewood, MN).

Systems and methods for treating an aqueous solution to reduce ammonia
25 concentration are disclosed herein. Reducing ammonia concentration may include removing any amount of ammonia from the aqueous stream. Thus, in some embodiments, ammonia concentration may be reduced by at least 10%, for example, at least 25%, at least 50%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%. Systems and methods for recovery of ammonia are disclosed herein. Recovery
30 of ammonia may include transferring nitrogen-containing compounds from an aqueous solution into an acidic solution. Rate of recovery of ammonia, as used herein, may refer to a rate of transfer of nitrogen-containing compounds. In some embodiments, at least 10% of ammonia may be recovered from the aqueous solution, for example, at least 25%, at least

50%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%.

The methods may include directing the aqueous solution comprising ammonia to a module comprising a plurality of membranes, each membrane having a shell side and a lumen side. The aqueous solution may be directed to a shell inlet of the module. An acidic solution may be directed to a lumen inlet of the module. As the aqueous solution flows along the shell side of the membranes, ammonia is generally filtered through the membrane into the acidic solution traveling in a countercurrent direction through the lumen. The reaction may produce an effluent having reduced ammonia, which is discharged through the shell outlet of the module and an intermediate product comprising ammonium, which is discharged through the lumen outlet of the module.

The membrane may be formed of a hydrophobic material. In some embodiments, the membrane may be formed of a hydrophobic polymeric material or combination of hydrophobic polymeric materials. Exemplary hydrophobic polymeric materials include polypropylene, polyethylene, polystyrene, polyvinylchloride, polytetrafluorethylene, polydimethylsiloxane, polyester, and polyurethane. The membrane and/or module may be operable at high temperatures. In some embodiments, the membrane and/or module may be operable at a temperature of 95°F (35°C) or greater, for example, 95°F (35°C) – 150°F (65.55°C) or 158°F (70°C). Thus, in some embodiments, the membrane and/or module may also be operable at a temperature of 120°F (48.89°C) – 150°F (65.55°C) or alternatively 122°F (50°F) – 158°F (70°C).

In some embodiments, the method may be performed with a plurality of modules arranged in series. The aqueous solution may be directed to the shell inlet of a lead module in the series. The acidic solution, which generally runs countercurrent to the aqueous solution, may be directed to an end module in the series, the end module being positioned opposite or farthest from the lead module in the series. Optionally, one or more intermediate modules may be positioned in the series between the lead module and the end module.

As the aqueous solution is directed to the lead module, an effluent having a lower concentration of ammonia is generally produced which may be discharged through the shell outlet of the lead module. The effluent may then be directed to a shell inlet of a following module in the series. Similarly, as the acidic solution is directed to the end module, an intermediate product having a higher concentration of ammonium is generally produced which may be discharged through the lumen outlet of the end module. At least a portion of the intermediate product (and optionally all of the intermediate product) may then be directed

to a lumen inlet of a preceding module in the series. In certain embodiments, an optional acidic stream may be combined with the intermediate product upstream from the lumen inlet of the preceding module. The lumen inlet and shell inlet may be positioned on opposite ends of the module. Thus, in operation, the aqueous solution and acidic solution may run
5 countercurrent to each other through the module. The lumen outlet and shell outlet may also be positioned on opposite ends of the module, each outlet positioned across from a respective inlet.

In certain exemplary embodiments, the acidic solution may comprise sulfuric acid (H_2SO_4), which dissociates into hydrogen ions (2H^+) and sulfate ions (SO_4^{2-}). The hydrogen
10 ions may react with ammonia ($\text{NH}_3(\text{g})$) transferred through the membrane to produce ammonium (NH_4^+). In this exemplary embodiment, the ammonium reacts with the sulfate ions to produce ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). Thus, in some embodiments, the intermediate product may comprise ammonium in the form of ammonium sulfate. In some embodiments, pH of the acidic solution may be controlled to optimize efficiency of the acidic solution. In
15 this exemplary embodiment, the pH of the acidic solution may be controlled to be below about 5.4, for example, between about 2 – 5.4, between about 3 – 5.4, between about 4 – 5.4, or between about 5 – 5.4. In some embodiments, pH of the acidic solution may be controlled to avoid the production of dihydrogen ions (H_2^+). In this exemplary embodiment, the pH of the acidic solution may be controlled to be below about 2, for example, between about 1.5 –
20 2, for example, between about 1.5 – 1.75 or between about 1.75 – 2, about 1.5, about 1.65, about 1.8, about 1.9, or about 2.

The disclosure relates to sulfuric acid as one exemplary acid for ammonia recovery. However, it should be understood that the methods and systems disclosed herein may utilize other acids for effective ammonia recovery. Exemplary acids which may be used instead of
25 sulfuric acid include phosphoric acid, citric acid, and others. Thus, in certain embodiments, the ammonium may react to produce ammonium phosphate, ammonium citrate, or others. The target pH range may be selected responsive to the acid. For instance, the target pH range may correspond to a pH range for which the acid will efficiently re-ionize and absorb ammonia, or the target pH range may correspond to a pH range to avoid production of
30 dihydrogen ions, as previously described.

Furthermore, in some embodiments, temperature of the reaction, for example, temperature of the aqueous solution and/or acidic solution, may be controlled. For instance, temperature of the aqueous solution and/or acidic solution may be controlled to be above about 95°F (35°C), for example, between about 95°F (35°C) – 150°F (65.55°C) or 158°F

(70°C), or between about 120°F (48.89°C) – 150°F (65.55°C) or alternatively 122°F (50°F) – 158°F (70°C). The elevated temperature may increase ammonia volatility, improving the efficiency of the reaction. In some embodiments, the temperature of the acidic solution may be controlled to be equal to or greater than the temperature of the aqueous solution. For instance, in some embodiments, the temperature of the acidic solution may be controlled to be equal to, or at least 1°F greater, or at least 0.5°C greater, than the temperature of the aqueous solution, for example, 0-1°F, 0-5°F, 1-10°F, 1-20°F greater or more, or 0-0.5°C, 0-2.5°C, 1-2.5°C, 1-5°C, 1-10°C, or more. While not wishing to be bound by theory, it is believed that controlling this temperature differential may prevent condensation within the module, which is generally undesirable.

The effluent, produced from the aqueous solution after removal of ammonia, may be directed to a point of use. The point of use may be associated with an industrial, commercial, or consumer use. The point of use may be associated with microelectronics manufacturing, semiconductor manufacturing, food and beverage production, food processing (including agricultural uses and irrigation), power and steam generation (including nuclear power generation), oil and gas processing, textile manufacturing, paper manufacturing and recycling, pharmaceutical manufacturing, chemical processing, laboratory and analytical uses, inks and coatings, metal extraction systems or processes, and others.

In certain exemplary embodiments, for an aqueous solution comprising about 6000 ppm ammonia nitrogen ($\text{NH}_3\text{-N}$), the effluent may comprise 155 ppm or less $\text{NH}_3\text{-N}$ (200 mg/L NH_4). In certain exemplary embodiments, aqueous solutions treatable by the methods disclosed herein may comprise 300 ppm-8000 ppm $\text{NH}_3\text{-N}$, for example, 300-500 ppm, 500-1000 ppm, 1000-2000 ppm, 2000-4000 ppm, 4000-6000 ppm or 6000-8000 ppm. However, aqueous solutions having less than 300 ppm $\text{NH}_3\text{-N}$ may also be treatable by the methods disclosed herein.

The effluent produced by the systems and methods described herein may have 80-99% less $\text{NH}_3\text{-N}$, for example, 80-85% less, 85-90% less, 90-95% less, 95-97% less, or 97-99% less $\text{NH}_3\text{-N}$ than the aqueous solution. In certain embodiments, at least 80-99% ammonia may be recovered from the aqueous solution, for example, at least 80-85%, at least 85-90%, at least 90-95%, at least 95-97%, or at least 97-99% ammonia may be recovered from the aqueous solution. In some embodiments, the efficiency of ammonia recovery may be at least 50%, for example, at least 60%, at least 70%, at least 80%, at least 85%, at least 90%, at least 95%, or at least 99%.

Thus, in certain exemplary embodiments, the effluent may comprise a target ammonia concentration of 1-200 ppm $\text{NH}_3\text{-N}$, for example, 1-15 ppm, 15-25 ppm, 25-40 ppm, 40-70 ppm, 70-100 ppm, 100-125 ppm, 125-145 ppm, 145-155 ppm, 155-165 ppm, 165-175 ppm, 175-185 ppm, or 185-200 ppm $\text{NH}_3\text{-N}$. In accordance with certain embodiments, the method
5 may be performed to produce an effluent having less than a threshold concentration of ammonia. The threshold concentration may be between 1-200 ppm $\text{NH}_3\text{-N}$, for example 1 ppm, 15 ppm, 25 ppm, 40 ppm, 50 ppm, 60 ppm, 70 ppm, 100 ppm, 125 ppm, 135 ppm, 145 ppm, 155 ppm, 165 ppm, 175 ppm, 185 ppm, or 200 ppm $\text{NH}_3\text{-N}$.

In some embodiments, the wastewater to be treated, for example, the raw wastewater,
10 may be directed to a reservoir. Within the reservoir, the wastewater may reach equilibrium, for example, producing an aqueous solution which is substantially homogeneous. The reservoir may allow the aqueous solution to be circulated through the module(s) at a constant flow rate and with a substantially consistent composition. The raw wastewater may be associated with an industrial, manufacturing, agricultural, laboratory, or wastewater
15 processing facility. In certain exemplary embodiments, the raw wastewater may be associated with a biological treatment process, for example, a methanogenesis treatment process. Thus, in some embodiments, the aqueous solution may be substantially homogeneous.

The methods may comprise measuring one or more property, for example, of the aqueous solution, acidic solution, acid, product, effluent, intermediate product, or within the
20 system. The property may be measured within a reservoir or in-line. The methods may comprise measuring one or more of temperature, pH, pressure, density, specific gravity, conductivity, turbidity, total suspended solids (TSS), total organic carbon (TOC), ammonia concentration (nitrogen concentration), concentration of a contaminant, such as an inorganic constituent, or others. Other parameters that may be measured include, but are not limited to,
25 H_2O_2 concentration, O_2 concentration, or CO_2 concentration.. In certain exemplary embodiments, inorganic constituents may be measured, for example, to determine whether the concentration may be present at or near solubility limit may be measured. Exemplary inorganic constituents include calcium, magnesium, aluminum, iron, silicon dioxide, or others.

30 In certain exemplary embodiments, the methods may comprise measuring one or more property of the aqueous solution or effluent selected from pH, temperature, and level of saturation of certain contaminants, such as inorganic contaminants. If the level of contaminants is too high, the methods may include removing contaminants to avoid or reduce scaling of the membrane and allow for efficient pH control.

In certain exemplary embodiments, the methods may comprise measuring one or more property of the acidic solution or intermediate product selected from pH, temperature, density, specific gravity, conductivity, concentration of the acid, ammonia concentration (nitrogen concentration), or ionic concentration, for example, sulfate or phosphate
5 concentration. The methods may comprise adjusting the concentration of acid in the acidic solution responsive to the measured property.

In accordance with certain exemplary embodiments, the methods may comprise measuring or determining ammonia concentration of the raw wastewater or aqueous solution. In some embodiments, the methods may comprise measuring or determining ammonia
10 concentration of an effluent. Ammonia concentration may be measured with an ammonia nitrogen sensor. In some embodiments, the methods may comprise measuring or determining ammonium concentration of an intermediate product. Ammonium concentration of the intermediate product may be measured or determined by measuring one or more of pH, density, and conductivity of the intermediate product. A correlation may be drawn between
15 an increasing ammonium concentration in the intermediate product and a decreasing concentration of ammonia in the aqueous solution or effluent. Thus, the methods may comprise determining a rate of ammonia recovery from the aqueous solution.

One or more parameter of the system may be adjusted responsive to rate of ammonia recovery. In some embodiments, flow rate, pH or temperature may be adjusted to increase or
20 decrease a rate of ammonia recovery. For instance, flow rate of one or more of the aqueous solution and effluent or the acidic solution and intermediate product may be independently adjusted to increase or decrease a rate of ammonia recovery. Temperature is believed to have a direct relationship with rate of ammonia recovery, at least until a threshold temperature is reached. Thus, it is believed that increasing temperature will generally increase a rate of
25 ammonia recovery until a target rate of ammonia recovery is achieved. Additionally, in some embodiments, pH of the acidic solution may be adjusted to increase or decrease a rate of ammonia recovery. For instance, pH of the acidic solution or aqueous solution may be adjusted to be within a target range (as described in more detail below) to increase the rate of ammonia recovery.

30 The ammonium, for example generated from the reaction within the module may be used in the manufacture of an ammonium product, such as a fertilizer product. For instance, ammonium sulfate, ammonium phosphate, ammonium citrate, or other ammonium compounds, may be useful as a fertilizer composition containing both nitrogen and other compounds, such as sulfur. In some embodiments, the ammonium product may be in a liquid

fertilizer form. In other embodiments, the ammonium product may be crystalized into a dried fertilizer form. For example, in some embodiments, the method may comprise drying the ammonium product to produce a dried fertilizer.

Thus, in some embodiments, at least a fraction of the intermediate product comprising ammonium may be collected as a product and used to manufacture an ammonium product, such as a fertilizer product. The intermediate product may be collected downstream from the end module, for example, downstream from a lumen outlet of the end module. The intermediate product may be collected downstream from an intermediate module, for example, downstream from a lumen outlet of an intermediate module. The intermediate product may be collected downstream from the lead module, for example, downstream from a lumen outlet of the lead module.

In some embodiments, at least a fraction of the intermediate product may be recirculated to generate the acidic solution. For instance, the intermediate product may be directed back to a reservoir utilized as the source of the acidic solution. An acid may be combined with the intermediate product to produce the acidic solution. The acid may be combined with the intermediate product in an amount effective to maintain a target pH or pH range of the acidic solution. In exemplary embodiments, sulfuric acid may be introduced into the reservoir in an effective amount to maintain the target pH or pH range of the acidic solution. For instance, sulfuric acid may be added to the reservoir, while an equivalent amount of acidic solution is purged from the reservoir. The exemplary acidic solution may, in certain embodiments, be maintained with less than 35% ammonium sulfate, for example, within 20-35% ammonium sulfate, for example, 20-25%, 25-30%, or 30-35% ammonium sulfate. The acidic solution may be maintained with at least 10% sulfuric acid, for example, within 10%-14% sulfuric acid.

In some embodiments, a product comprising ammonium, for example, ammonium sulfate, may be withdrawn from the reservoir. The product withdrawn from the reservoir may be used to generate an ammonium product, such as a fertilizer product, as previously described. In other embodiments, the product withdrawn from the reservoir may be purged. In some embodiments, the acid and product are introduced and withdrawn from the reservoir in a continuous mode. In other embodiments, the acid and product are introduced and withdrawn from the reservoir in a batch mode. By producing the acidic solution in the reservoir for recirculation, the solution may reach equilibrium, for example, the acidic solution may be substantially homogeneous, allowing the acidic solution to be circulated through the module(s) at a constant flow rate and with a substantially consistent composition.

Thus, the systems and methods disclosed herein may be used to efficiently produce an ammonium product and an effluent having a low concentration of ammonia.

In some embodiments, flow rate of the aqueous solution and/or acidic solution may be controlled. The methods may comprise directing the aqueous solution to the module at an exemplary flow rate of between about 150-250 mL/min, for example, 150-175 mL/min, 175-185 mL/min, 185-200 mL/min, 200-225 mL/min, or 225-250 mL/min. The methods may comprise directing the acidic solution to the module at a flow rate at least 2-10 times faster than the flow rate of the aqueous solution. In some embodiments, the acidic solution may be directed to the module at an exemplary flow rate of between about 1,000-1,500 mL/min, for example, 1,000-1,100 mL/min, 1,100-1,200 mL/min, 1,200-1,300 mL/min, 1,300-1,400 mL/min, or 1,400-1,500 mL/min. It should be understood that flow rate may generally be scaled with module size. Thus, higher flow rates (for example, greater than the exemplary flow rates of 250 mL/min or 1,500 mL/min) may be utilized with larger modules.

FIG. 1 is a box diagram of a system 1000 for recovering ammonia from an aqueous solution. The system 1000 may comprise a plurality of modules, including a lead module 110 and an end module 130 positioned in series. In certain embodiments, the system may have 2-5 modules arranged in series, for example, 2 modules, 3 modules, 4 modules, or 5 modules. The exemplary system 1000 of FIG. 1 includes one intermediate module 120 positioned between the lead module 110 and the end module 130, however the system may be free of intermediate modules 120 or may comprise more than one intermediate module 120.

The system 1000 may include a source of an aqueous solution 210 fluidly connected to the modules 110, 120, 130 in series. In particular, the source of the aqueous solution 210 may be directly fluidly connected to the lead module 110. The system 1000 may include a source of an acidic solution 310 fluidly connected to the modules 110, 120, 130 in series. In particular, the source of the acidic solution 310 may be directly fluidly connected to the end module 130. In certain embodiments, the source of the acidic solution 310 may be fluidly connected to additional modules, for example, to the lead module 110 or an intermediate module 120 (shown in dashed lines in FIG. 1). The acidic solution may optionally be directed to the additional module as required to control pH of the acidic solution at the module. Each module 110, 120, 130 may produce an effluent by removing ammonia from the aqueous solution. Each module 110, 120, 130 may produce an intermediate product comprising ammonium.

The source of the aqueous solution 210 and/or the source of the acidic solution 310 may comprise reservoirs. The system 1000 may produce an effluent, which is optionally

directed to an effluent reservoir 220. The system 1000 may include a return conduit fluidly connecting the modules 110, 120, 130 back to the source of the acidic solution 310. In certain embodiments, the system 1000 may include one or more draw lines to collect a portion of the intermediate product downstream from a module 110, 120, 130, and upstream from the source of the acidic solution 310. The system 1000 may produce a product, either from the one or more draw lines or from the acidic solution reservoir 310, which is optionally directed to a product reservoir 320. The system 1000 may include a source of an acid 330 fluidly connected to the source of the acidic solution 310. The source of the acidic solution 310 may include a discharge outlet. In the exemplary embodiment of FIG. 1, the discharge outlet is fluidly connected to optional product reservoir 320. In some embodiments, a source of raw wastewater (not shown) may be fluidly connected to the source of the aqueous solution 210.

The source of the aqueous solution 210 may be fluidly connected to a shell inlet of the lead module 110. The lead module 110 may produce a first effluent from the aqueous solution through the shell side. The shell outlet of the lead module 110 may be fluidly connected to the shell inlet of the intermediate module 120 and end module 130. In exemplary system 1000, the shell outlet of the lead module 110 is fluidly connected to the shell inlet of the end module 130 via the intermediate module 120. Thus, the shell outlet of the lead module 110 may be fluidly connected to direct the first effluent to the shell inlet of the intermediate module 120, while the shell outlet of the intermediate module 120 may be fluidly connected to direct a second effluent to the shell inlet of the end module 130. The shell outlet of the end module 130, from which a final effluent may be produced, may be fluidly connected to the effluent reservoir 220.

The source of the acidic solution 310 may be fluidly connected to a lumen inlet of the end module 130. The end module 130 may produce a first intermediate product through the lumen side. In general, the acidic solution and intermediate product may be directed through each module 110, 120, 130 in a countercurrent direction opposite the aqueous solution and effluent. The lumen outlet of the end module 130 may be fluidly connected to the lumen inlet of the intermediate module 120 and the lead module 110.

In exemplary system 1000, the lumen outlet of the end module 130 is fluidly connected to the lumen inlet of the lead module 110 via the intermediate module 120. Thus, the lumen outlet of the end module 130 may be fluidly connected to direct the first intermediate product to the lumen inlet of the intermediate module 120, while the lumen outlet of the intermediate module 120 may be fluidly connected to direct a second intermediate product to the lumen inlet of the lead module 110.

The lumen outlet of the first module 110, from which the third intermediate product may be produced, may be fluidly connected to the product reservoir or to the source of the aqueous solution 310 via a return conduit. In some embodiments, as previously described, the intermediate product may be dosed with acidic solution to control pH. Furthermore, in some
5 embodiments, at least some of the intermediate product may be drawn between modules for collection as an ammonia product, such as a fertilizer product.

In certain embodiments, the system may comprise a plurality of rows, each row including a plurality of modules. The plurality of modules in each row may be arranged in series. The plurality of rows may be arranged in parallel. In certain embodiments, the system
10 may comprise 2-10 rows, for example, 2 rows, 3 rows, 4 rows, 5 rows, 6 rows, 7 rows, 8 rows, 9 rows, or 10 rows. The number of rows may be scaled, for example, to include more than 10 rows. Each row may include 2-5 modules in series, as previously described with respect to exemplary system 1000.

FIG. 2 is a box diagram showing an exemplary system 2000 including a plurality of
15 rows. A first row of system 2000 includes lead module 110A and end module 130A. The first row of system 2000 includes intermediate module 120A. Each row may be free of an intermediate module 120A or include more than one intermediate module 120A. A second row of system 2000 includes lead module 110B and end module 130B. The second row of system 2000 includes intermediate module 120B. The number of modules in each row may
20 be the same, as shown in system 2000, or different. Thus, in certain embodiments, the number of modules in each row may be independently selected.

The plurality of modules 110A, 120A, 130A are arranged in series, as previously described with respect to system 1000. Furthermore, the plurality of modules 110B, 120B, 130B are arranged in series, as previously described with respect to system 1000. In
25 exemplary system 2000, each lead module 110A, 110B is independently fluidly connected to the source of the aqueous solution 210 through a respective shell inlet. Similarly, in exemplary system 2000, each end module 130A, 130B is independently fluidly connected to the source of the acidic solution 310 through a respective lumen inlet. In exemplary system 2000, each end module 130A, 130B is fluidly connected to an effluent reservoir 220 through
30 a respective shell outlet. Finally, in exemplary system 2000, each lead module 110A, 110B is fluidly connected to the source of the acidic solution 310 by a return conduit fluidly connected to each respective lumen outlet.

While exemplary system 2000 includes a common source of the aqueous solution 210, source of the acidic solution 310, and effluent reservoir 220 for all rows, it should be

noted that, in other embodiments, each row may include independent reservoirs for one or more of the source of the aqueous solution 210, the source of the acidic solution 310, and the optional effluent reservoir 220. In other embodiments, a fraction of the rows may be fluidly connected to common reservoirs. For example, 2-10 rows may be connected to a common
5 source of the aqueous solution 210, source of the acidic solution 310, and/or effluent reservoir 220. In such embodiments, the system may further be scaled up by including a plurality of each reservoir of the source of the aqueous solution 210, the source of the acidic solution 310, and/or the effluent reservoir 220. The number of rows fluidly connected to each reservoir may be independently selected.

10 In some embodiments, the system may include one or more flow control subsystems configured to control flow rate of the aqueous solution and/or the source of the acidic solution. For instance, the system may include a flow control subsystem configured and arranged to control flow rate of the aqueous solution and effluent through the modules. The system may include a flow control subsystem configured and arranged to control flow rate of
15 the acidic solution and intermediate product through the modules. In general, flow rates of the aqueous solution and effluent may be jointly controlled. Separately and independently, flow rates of the acidic solution and intermediate product may be jointly controlled. The flow control subsystems may be programmed to control flow rate to be within a target flow rate range as previously described.

20 FIG. 3 is a box diagram of an exemplary system 3000 including flow control subsystems. The flow control subsystems include pump 211 and pump 313. Pump 211 is positioned to control flow rate of the aqueous solution and effluent through the shell side of modules 110, 120, 130. Pump 313 is positioned to control flow rate of the acidic solution and intermediate product through the lumen side of modules 110, 120, 130 in a countercurrent
25 direction as the aqueous solution and effluent. In some embodiments, pumps 211 and 313 may be operably connected to controller 400. The controller 400 may be programmed to direct pumps 211 and/or 313 to control flow rate of the aqueous solution, effluent, acidic solution, and intermediate product through modules 110, 120, 130.

30 In certain embodiments, the flow control subsystem may comprise one or more flow meter. The flow meter may be positioned to measure flow rate of one or more of the aqueous solution, effluent, acidic solution, and intermediate product through the modules. The flow meter may be operably connected to one or both of pump 211 and pump 313. The pump 211 or pump 313 may be programmed to control flow rate responsive to a measurement received from the flow meter. In some embodiments, the flow meter and/or pump may be operably

connected to controller 400. The controller 400 may be programmed to direct one or both of pump 211 and pump 313 to operate responsive to the measurement received from the flow meter.

5 In some embodiments, the system may include one or more temperature control subsystems. The temperature control subsystems may be programmed to control temperature of the aqueous solution and/or the acidic solution. In some embodiments, the temperature control subsystems may be programmed to control temperature to be within a target temperature range as previously described. The temperature control subsystem may additionally or alternatively be programmed to measure temperature of one or more of the
10 aqueous solution, an effluent, the acidic solution, an intermediate product, or the product. In some embodiments, the temperature control subsystem may be programmed to control temperature responsive to a temperature measurement.

Exemplary system 3000 includes a temperature control subsystem configured to control temperature of the aqueous solution. In particular, system 3000 includes heat
15 exchanger 260 positioned to heat or cool the aqueous solution within reservoir 210. Sensor 240 may be configured to measure temperature of the aqueous solution within reservoir 210. In some embodiments, heat exchanger 260 is operably connected to sensor 240. Heat exchanger 260 may be programmed to control temperature of the aqueous solution responsive to a measurement of temperature received from sensor 240. In some embodiments, one or
20 both of heat exchanger 260 and sensor 240 may be operably connected to controller 400. Controller 400 may be programmed to direct the heat exchanger 260 to control temperature of the aqueous solution, optionally responsive to a measurement of temperature received from sensor 240.

While exemplary system 3000 includes a temperature control subsystem configured to
25 control temperature of the aqueous solution, it should be understood that the system may include an alternative or additional temperature control subsystem (including a heat exchanger and or temperature sensor) programmed to control temperature of the acidic solution.

In some embodiments, the system may include one or more pH control subsystems.
30 The pH control subsystems may include a source of an acid and/or a source of a base fluidly connected to the aqueous solution and/or the acidic solution. The pH control subsystems may be programmed to control pH of the aqueous solution and/or the acidic solution. In some embodiments, the pH control subsystems may be programmed to control pH to be within a target pH range as previously described. The pH control subsystem may additionally or

alternatively be programmed to measure pH of one or more of the aqueous solution, an effluent, the acidic solution, an intermediate product, or the product. In some embodiments, the pH control subsystem may be programmed to control pH responsive to a pH measurement.

5 Exemplary system 3000 includes a pH control subsystem configured to control pH of the acidic solution. The pH control subsystem includes source of an acid 330 and valves 331, 312. Valve 331 is positioned to control flow of the acid from reservoir 330 into the acidic solution reservoir 310. Valve 312 is positioned to control flow of the acidic solution from reservoir 310 through a discharge outlet to optional product reservoir 320. Valves 331, 312
10 may be programmed to introduce acid and remove acidic solution to maintain a target pH range within the reservoir 310. Sensor 340 may be configured to measure pH of the acidic solution within reservoir 310. In some embodiments, valves 331, 312 may be operably connected to sensor 340. The valves 331, 312 may be programmed to be actuated responsive to a measurement of pH received from the sensor 340. In some embodiments, one or more of
15 valve 331, valve 312, and sensor 340 may be operably connected to controller 400. Controller 400 may be programmed to direct the valves 331, 312 to control pH of the acidic solution, optionally responsive to a measurement of pH received from sensor 340.

While exemplary system 3000 includes a pH control subsystem configured to control pH of the acidic solution, it should be understood that the system may include an alternative
20 or additional pH control subsystem (including a source of an acid or a base, one or more valve, and/or a pH sensor) programmed to control pH of the aqueous solution. For example, the system may comprise a source of a base fluidly connected to the aqueous solution. In certain exemplary embodiments, the base may comprise sodium hydroxide (NaOH) as shown in FIG. 5. The base may be added to the aqueous solution in an amount effective to maintain
25 a target pH range, for example, to maintain a pH above 10, for example, between 10-12, for example, 10-10.5, 10.5-11, 11-11.5, or 11.5-12.

The system may include one or more of sensors 240, 340, 250, 350. As shown in exemplary system 3000, sensor 240 is positioned to measure a parameter of the aqueous solution, sensor 340 is positioned to measure a parameter of the acidic solution, sensor 250 is
30 positioned to measure a parameter of the effluent, and sensor 350 is positioned to measure a parameter of the product. The sensors 240, 340, 250, 350 may be configured to measure one or more of temperature, pH, density, conductivity, turbidity, specific gravity, total suspended solids (TSS), total organic carbon (TOC), H₂O₂ concentration, ammonia concentration, O₂ concentration, CO₂ concentration, or composition, for example, concentration of one or more

compound. It should be understood that sensors 240, 340, 250, 350 may be formed of a single sensor or multiple sensors, optionally each sensor configured to measure a different parameter.

While exemplary sensors 240, 340, 250, 350 of system 3000 are shown in
5 communication with reservoirs 210, 310, 220, 320, respectively, it should be understood that one or more of sensors 240, 340, 250, 350 may be positioned in-line in communication with a relevant conduit. Furthermore, the system may include a sensor positioned to measure a parameter of the intermediate product. The sensor configured to measure a parameter of the intermediate product may be in communication with a reservoir holding the intermediate
10 product or in-line in communication with the intermediate product return conduit.

Thus, in some embodiments, the system may include a controller 400. The controller may be operably connected to one or more flow control subsystem, for example, one or both of pump 211 and pump 313. The controller 400 may be operably connected to the temperature control subsystem, for example, heat exchanger 260. The controller 400 may be
15 operably connected to the pH control subsystem, for example, one or both of valve 331 and valve 312. Thus, the controller 400 may be programmed to control one or more of flow rate, temperature, and pH within the system. In some embodiments, the controller 400 may be operably connected to one or more of sensor 240, sensor 340, sensor 250, and sensor 350. The controller 400 may be programmed to control one or more of flow rate, temperature, and
20 pH responsive to a measurement received from one or more of sensor 240, sensor 340, sensor 250, and sensor 350. The controller 400 may be connected to the one or more components through a wireless connection. For example, the controller may be connected through wireless local area networking (WLAN) or short-wavelength ultra-high frequency (UHF) radio waves.

25 The controller 400 may be associated with one or more processors typically connected to one or more memory devices. The memory device may be used for storing programs and data during operation of the system. For example, the memory device may be used for storing historical data relating to the parameters over a period of time, as well as operating data. In some embodiments, the controller 400 disclosed herein may be operably connected to an
30 external data storage. For instance, the controller 400 may be operable connected to an external server and/or a cloud data storage. Thus, the controller 400 may be configured to transmit data to a memory storing device or a cloud-based memory storage. Such data may include, for example, operating parameters, measurements, and/or status indicators of the system components.

The stored data may be accessed through a computer or mobile device. In some embodiments, the controller 400 or a processor associated with the memory storage may be configured to notify a user of an operating parameter, measurement, and/or status of the system components. For instance, a notification may be pushed to a computer or mobile
5 device notifying the user. Operating parameters and measurements include, for example, properties of the aqueous solution, acidic solution, effluent, intermediate product, or product. Status of the system components may include, for example, status of one or more sensor, pump, or valve, such as whether the system component is offline (disconnected from the controller 400), has lost power, requires adjustment, requires maintenance (planned or
10 unplanned maintenance), and/or fill level of a reservoir. However, the notification may relate to any operating parameter, measurement, or status of a system component disclosed herein. In certain embodiments, information, such as system updates, may be transmitted to the controller 400 from an external source.

The controller 400 may further be configured to access data from the memory storing
15 device or cloud-based memory storage. The controller 400 may be programmed to predict operation of the system based on historical data stored in the memory storage. For instance, the controller 400 may be programmed to predict future adjustments required to the flow control, temperature control, or pH control based on current measured parameters and historical data. The controller 400 may additionally be programmed to predict whether a
20 system component will require adjustment or maintenance based on current measured parameters and historical data. In some embodiments, one or more of the processes disclosed herein may be manually or semi-automatically executed.

In some embodiments, the system may comprise one or more manifold configured to distribute fluid streams. FIG. 4 is a box diagram showing an exemplary system 4000
25 including a first row of modules 110A, 120A, 130A and second row of modules 110B, 120B, 130B. The exemplary system 4000 includes manifolds 115, 215, 315 positioned to distribute fluid streams. In particular, manifold 115 is positioned to integrate a first intermediate product from module 110A and a second intermediate product from module 110B into a return conduit directed to the acidic solution reservoir 310. Manifold 215 is positioned to distribute
30 aqueous solution from the source of the aqueous solution 210 to module 110A and module 110B. Manifold 315 is positioned to distribute acidic solution from the source of the acidic solution 310 to module 130A and module 130B. Manifolds 115, 215, 315 may be operably connected to controller 400. Thus, in some embodiments, controller 400 may be programmed

to control distribution of one or more flow streams within the system by actuating one or more of manifold 115, manifold 215, and manifold 315.

In some embodiments, one or more separation device or filter, for example, cartridge filter (FIG. 5), may be used to collect unwanted contaminants, such as scale-forming agents, debris, or other contaminants, from the aqueous solution, effluent, acidic solution, intermediate product, or product. For instance, a separation device or filter may be positioned to separate contaminants that may otherwise collect or form scale on the membrane. In certain exemplary embodiments, the filter may be a 5 micron cartridge filter. The separation device or filter may be positioned downstream from the source of the aqueous solution or downstream from the source of the acidic solution. In some embodiments, the separation device or filter may be positioned downstream from the shell outlet of the end module. In some embodiments, the separation device or filter may be positioned downstream from the lumen outlet of the lead module. In some embodiments, the separation device or filter may be positioned downstream from the discharge outlet of the source of the acidic solution.

In some embodiments, the system may include a source of a catalyst, such as a hydrogen peroxide (H_2O_2) destroying catalyst, fluidly connected to the source of the aqueous solution or an effluent. One exemplary catalyst is optimase (FIG. 5). For semiconductor manufacturing systems, an H_2O_2 destroying catalyst may be beneficial to degrade H_2O_2 in the aqueous solution or effluent.

FIG. 5 is a schematic diagram of a benchtop system for recovering ammonia from an aqueous solution, as used in the tests of the examples below. The system of FIG. 5 includes a feed source of an aqueous solution comprising ammonia. For the purposes of the benchtop experiments, the aqueous solution was optionally spiked ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and hydrogen peroxide (H_2O_2). Optimase and sodium hydroxide (NaOH) are fluidly connected to the raw wastewater in a feed tank maintained at 95°F (35°C). A first pump directs the aqueous solution to a cartridge filter positioned upstream from the lead module, module A. Three modules, module A, module B, and module C are positioned in series with respect to the aqueous solution. Each module contains a respective sampling valve. An effluent tank is positioned downstream from module C. A recycle conduit connects module B and module C to a tank storing the acidic solution. Sulfuric acid (H_2SO_4) is directed to the acidic solution tank, which is also maintained at 95°F (35°C). A second pump directs the acidic solution to a cartridge filter positioned upstream from the modules, which are arranged in parallel with respect to the acidic solution.

Examples

The function and advantages of these and other embodiments can be better understood from the following examples. These examples are intended to be illustrative in nature and are not considered to be limiting the scope of the invention.

5

Example 1: Benchtop Test using Aqueous Solution Spiked with Ammonium Sulfate ((NH₄)₂SO₄)

Preparation of Aqueous Solution

A batch of aqueous solution (60L) was prepared by spiking the sample with ammonium sulfate (758 g, at 12.6 g/L) to more closely resemble a maximum ammonia concentration from NH₄F of known historical samples. The solution was adjusted to a pH of 11.3 with sodium hydroxide. The ammonia concentration target was 4,600 mg/L N, equivalent to approximately 6,000 mg/L NH₄⁺. However, the actual ammonia concentration in the aqueous feed solution was determined to be 4,181 mg/L N after analysis.

15

Preparation of Acidic Solution

A batch of acidic solution (19L) was prepared by combining a synthetic ammonium sulfate solution from a previous test (to resemble steady state operating conditions) with sulfuric acid (0.95 g/L) dosing to reach a pH of 1.65.

20

Operating Parameters

The exemplary system of FIG. 5 was operated according to the parameters shown in Table 1 below. The modules were Liqui-CelTM Membrane contactors (distributed by 3MTM, Maplewood, MN) having dimensions of 2.5 in diameter by 8 in length and a membrane contact area of 16 ft². The cartridge filters were 5 micron cartridge filters.

25

30

Table 1: Operating Parameters

Aqueous Solution		
Tank temperature	95	°F
Flow rate	190	mL/min
pH	11.3	SU
Acidic Solution		
Tank temperature	95	°F
Flow rate	1,350	mL/min
pH	1.65	SU

The pilot unit processed about 46 liters of aqueous solution over a period of 4 hours.

Operating data was collected, and grab samples were taken from the reservoirs every 30 minutes.

5

Test Results

The results are presented in Table 2 below and in the graph of FIG. 6.

Table 2: Test Results for Benchtop Test with Ammonium Sulfate

Sample	pH (SU)	Ammonia (mg/L N)	Ammonium sulfate* (%)	Fluoride (mg/L)	H ₂ SO ₄ ** (g/L)
Feed tank, initial	11.4	4,181	-	3,069	-
Effluent tank, final	11.5	100	-	3,069	-
Acidic solution tank, initial	1.7	17,804	8.0	<0.2	-
Acidic solution tank, final	1.7	27,036	11.9	<0.2	-
Acid dosing, added	-	-	-	-	32.1

10 * Percent by weight based on ammonia analysis

**Cumulative dose of supplemental H₂SO₄ to maintain pH 1.7 in the acidic solution

As shown in Table 2, the membrane contactor unit removed 97.6% of the ammonia nitrogen from the aqueous solution containing 4,181 mg/L $\text{NH}_3\text{-N}$ and produced an effluent containing 100 mg/L $\text{NH}_3\text{-N}$ (129 mg/L NH_4). The membrane contactor pilot unit thus met an effluent quality target of 155mg/L $\text{NH}_3\text{-N}$ (200 mg/L NH_4). Table 2 also shows that fluoride was rejected by the membrane (< 0.2 mg/L F in the final acidic solution) as ammonia concentration increased from 17,804 to 27,036 mg/L N in the acidic solution tank.

A 97.6% ammonia recovery efficiency from 46 liters of aqueous solution containing 4,181 g/L $\text{NH}_3\text{-N}$ would be expected to add 9,919 mg/L $\text{NH}_3\text{-N}$ to 18.9 liters of the acid scrubbing solution. Table 2 shows that the ammonia concentration increased by 9,232 mg/L $\text{NH}_3\text{-N}$, which is 93% of the expected recovery.

The basicity of the effluent and acidity of the acidic solution stream immediately downstream from the lead module were determined to be adequate for ammonia removal from the aqueous solution. As shown in the graph of FIG. 6, the percentages of ammonia removal for the three membrane contactor modules were relatively stable over the time period of the test. The average ammonia removal rates were 83%, 67%, and 52% for the lead, intermediate (middle), and end (lag) modules, respectively.

Accordingly, under the tested parameters, the benchtop system was capable of meeting a target final ammonia concentration in the effluent tank of 200 mg/L NH_4 or less (actual final ammonia concentration was 129 mg/L NH_4). This test shows the ability of the system to remove ammonia from the aqueous solution while utilizing a countercurrent recirculated acidic solution at steady state with the addition of sulfuric acid as needed to maintain a desired pH range.

Example 2: Benchtop Test using Aqueous Solution without Ammonium Sulfate ($(\text{NH}_4)_2\text{SO}_4$)

A second test was performed under identical conditions as example 1 and using the exemplary system of FIG. 5, except that the aqueous solution was not spiked with ammonium sulfate. The aqueous solution had an actual ammonia concentration of 1,910 mg/L N. The acidic solution was prepared by dosing the remaining acidic solution from example 1 (to resemble steady state operating conditions) with an effective amount of sulfuric acid to reach a pH of 1.65.

Test Results

The results are presented in Table 3 below and in the graph of FIG. 7.

Table 3: Test Results for Benchtop Test without Ammonium Sulfate

Sample	pH (SU)	Ammonia (mg/L N)	Ammonium sulfate* (%)	Fluoride (mg/L)	H ₂ SO ₄ ** (g/L)
Feed tank, initial	11.3	1,910	-	3,069	-
Effluent tank, final	11.6	41	-	3,069	-
Acidic solution tank, initial	1.7	28,835	12.6	<0.2	-
Acidic solution tank, final	1.7	31,807	13.9	<0.2	-
Acid dosing, added	-	-	-	-	16.0

5 * Percent by weight based on ammonia analysis

**Cumulative dose of supplemental H₂SO₄ to maintain pH 1.7 in the acidic solution

As shown in Table 3, the membrane contactor unit removed 97.8% of the ammonia nitrogen from the aqueous solution containing 1,910 mg/L NH₃-N and produced an effluent containing 41 mg/L NH₃-N (53 mg/L NH₄). The membrane contactor pilot unit met an effluent quality target of 155 mg/L NH₃-N (200 mg/L NH₄). Table 3 also shows that all fluoride was rejected by the membrane (< 0.2 mg/L F in the final acidic solution) as ammonia concentration increased from 28,838 to 31,807 mg/L N in the acidic solution tank.

A 97.8% ammonia recovery efficiency from 46 liters of aqueous solution containing 1,910 g/L NH₃-N would be expected to add 4,608 mg/L NH₃-N to 18.9 liters of the acidic scrubbing solution. However, Table 3 shows that the ammonia concentration increased by 2,972 mg/L NH₃-N in the acidic solution, which is only 64% of the expected recovery.

The basicity of the effluent and acidity of the acidic solution stream immediately downstream from the lead module were determined to be adequate for ammonia removal

from the aqueous solution. As shown in the graph of FIG. 7, the percentages of ammonia removal for the three membrane contactor modules were relatively stable over the time period of the test. The average ammonia removal rates were 73%, 76%, and 64% for the lead, intermediate (middle), and end (lag) modules, respectively.

5 Accordingly, under the parameters of the second test, the benchtop system was capable of meeting a target final ammonia concentration in the effluent tank of 200 mg/L NH_4 or less (actual final ammonia concentration was 53 mg/L NH_4). This test shows the ability of the system to remove ammonia from the aqueous solution (having a lower ammonia nitrogen concentration) while utilizing a countercurrent recirculated acidic solution at steady
10 state with the addition of sulfuric acid as needed to maintain a desired pH range.

Example 3: Benchtop Test using Aqueous Solution and Acidic Solution Spiked with Ammonium Sulfate ($(\text{NH}_4)_2\text{SO}_4$)

 A third test was performed under identical conditions as example 1 and using the
15 exemplary system of FIG. 5, except that the acidic solution was also spiked with ammonium sulfate. The aqueous solution had an actual ammonia concentration of 4,653 mg/L N. The acidic solution was prepared by adding ammonium sulfate to the remaining acidic solution from example 2 to reach 25% (2,328 g $(\text{NH}_4)_2\text{SO}_4$ (123 g/L)) and dosing the solution with an effective amount of sulfuric acid to reach a pH of 1.65. Ammonium sulfate in the acidic
20 solution increased from 25.5% to 31.8% during the test.

Test Results

 The results are presented in Table 4 below and in the graph of FIG. 8.

25

30

Table 4: Test Results for Benchtop Test with Ammonium Sulfate in Aqueous Solution and Acidic Solution

Sample	pH (SU)	Ammonia (mg/L N)	Ammonium sulfate* (%)	Fluoride (mg/L)	H ₂ SO ₄ ** (g/L)
Feed tank, initial	11.5	4,653	-	3,069	-
Effluent tank, final	11.9	145	-	3,069	-
Acidic solution tank, initial	1.7	62,088	25.5	<0.2	-
Acidic solution tank, final	1.7	79,627	31.8	<0.2	-
Acid dosing, added	-	-	-	-	36.3

* Percent by weight based on ammonia analysis

**Cumulative dose of supplemental H₂SO₄ to maintain pH 1.7 in the acidic solution

5

As shown in Table 4, the membrane contactor unit removed 96.9% of the ammonia nitrogen from the aqueous solution containing 4,653 mg/L NH₃-N and produced an effluent containing 145 mg/L NH₃-N (186 mg/L NH₄). The membrane contactor pilot unit met an effluent quality target of 155 mg/L NH₃-N (200 mg/L NH₄). Table 4 also shows that all fluoride was rejected by the membrane (< 0.2 mg/L F in the final acidic solution) as ammonia concentration increased from 62,088 to 79,627 mg/L N in the acidic solution tank.

The data in Table 4 also shows that the ammonia concentration in the acidic solution tank increased by 17,539 mg/L NH₃- N which represents a 158% recovery. This high recovery can result from an error as small as 4% in the initial and final ammonia readings in the acidic solution tank, which is an acceptable analytical error.

The basicity of the effluent and acidity of the acidic solution stream immediately downstream from the lead module were determined to be adequate for ammonia removal from the aqueous solution. As shown in the graph of FIG. 8, the percentages of ammonia removal for the three membrane contactor modules were relatively stable over the time

period of the test. The average ammonia removal rates were 72%, 66%, and 68% for the lead, intermediate (middle), and end (lag) modules, respectively.

Accordingly, under the parameters of the third test, the benchtop system was capable of meeting a target final ammonia concentration in the effluent tank of 200 mg/L NH₄ or less
5 (actual final ammonia concentration was 186 mg/L NH₄). This test shows the ability of the system to remove ammonia from the aqueous solution while utilizing a countercurrent recirculated acidic solution (having a greater ammonium concentration) at steady state with the addition of sulfuric acid as needed to maintain a desired pH range.

10 The phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. As used herein, the term “plurality” refers to two or more items or components. The terms “comprising,” “including,” “carrying,” “having,” “containing,” and “involving,” whether in the written description or the claims and the like, are open-ended terms, i.e., to mean “including but not limited to.” Thus, the use of such terms
15 is meant to encompass the items listed thereafter, and equivalents thereof, as well as additional items. Only the transitional phrases “consisting of” and “consisting essentially of,” are closed or semi-closed transitional phrases, respectively, with respect to the claims. Use of ordinal terms such as “first,” “second,” “third,” and the like in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element
20 over another or the temporal order in which acts of a method are performed, but are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

Having thus described several aspects of at least one embodiment, it is to be appreciated various alterations, modifications, and improvements will readily occur to those
25 skilled in the art. Any feature described in any embodiment may be included in or substituted for any feature of any other embodiment. Such alterations, modifications, and improvements are intended to be part of this disclosure and are intended to be within the scope of the invention. Accordingly, the foregoing description and drawings are by way of example only.

Those skilled in the art should appreciate that the parameters and configurations
30 described herein are exemplary and that actual parameters and/or configurations will depend on the specific application in which the disclosed methods and materials are used. Those skilled in the art should also recognize or be able to ascertain, using no more than routine experimentation, equivalents to the specific embodiments disclosed.

What is claimed is:

CLAIMS

1. A system for recovering ammonia from an aqueous solution, comprising:
a plurality of modules arranged in series, each module comprising a plurality of
5 membranes, each membrane having a lumen side and a shell side,
the plurality of modules comprising a lead module having a shell inlet fluidly
connected to a source of the aqueous solution comprising ammonia, a shell outlet, a lumen
inlet, and a lumen outlet,
the plurality of modules comprising an end module having a lumen inlet fluidly
10 connected to a source of an acidic solution, a lumen outlet, a shell inlet, and a shell outlet,
the shell outlet of the lead module being fluidly connected to the shell inlet of the end
module, and the lumen outlet of the end module being fluidly connected to the lumen inlet of
the lead module.
- 15 2. The system of claim 1, further comprising at least one intermediate module having a shell
inlet, a shell outlet, a lumen inlet, and a lumen outlet, the shell inlet of the intermediate
module being fluidly connected to the shell outlet of the lead module, the shell outlet of the
intermediate module being fluidly connected to the shell inlet of the end module, the lumen
inlet of the intermediate module being fluidly connected to the lumen outlet of the end
20 module, and the lumen outlet of the intermediate module fluidly connected to the lumen inlet
of the lead module.
3. The system of claim 1, wherein the aqueous solution is substantially homogeneous.
- 25 4. The system of claim 3, further comprising a temperature control subsystem configured to
control temperature of the aqueous solution.
5. The system of claim 3, further comprising at least one sensor configured to measure at
least one property of the aqueous solution selected from temperature pH, ammonia
30 concentration, or concentration of a contaminant.
6. The system of claim 6, wherein the lumen outlet of the lead module is fluidly connected to
a reservoir comprising the source of the acidic solution by a return conduit.

7. The system of claim 6, wherein the reservoir comprises an inlet fluidly connectable to a source of an acid and a discharge outlet.
8. The system of claim 7, further comprising at least one sensor configured to measure at least one property of the acidic solution selected from temperature, pH, density, specific gravity, conductivity, ammonia concentration, concentration of the acid, or ionic concentration.
9. The system of claim 7, further comprising a pH control subsystem configured to control pH of the acidic solution.
10. The system of claim 1, further comprising a flow control subsystem configured to control flow rate of the aqueous solution.
11. The system of claim 1, further comprising a flow control subsystem configured to control flow rate of the acidic solution.
12. The system of claim 1, wherein the plurality of membranes are hydrophobic and the module is operable at a temperature of 120°F – 150°F.
13. A system for recovering ammonia from an aqueous solution, comprising:
a plurality of rows arranged in parallel, each row comprising a plurality of modules arranged in series, each module comprising a plurality of membranes, each membrane having a lumen side and a shell side,
each lead module of the row having a shell inlet fluidly connected to a source of the aqueous solution comprising ammonia, a lumen inlet, a shell outlet, and a lumen outlet,
each end module of the row having a lumen inlet fluidly connected to a source of an acidic solution, a lumen outlet fluidly connected to the lumen inlet of the corresponding lead module, a shell inlet fluidly connected to the shell outlet of the corresponding lead module, and a shell outlet,
the lumen outlet of each lead module being fluidly connected to the source of the acidic solution by a return conduit.

14. The system of claim 13, wherein each row further comprises at least one intermediate module having a shell inlet, a shell outlet, a lumen inlet, and a lumen outlet, the shell inlet of the intermediate module being fluidly connected to the shell outlet of the corresponding lead module, the shell outlet of the intermediate module being fluidly connected to the shell inlet of the corresponding end module, the lumen inlet of the intermediate module being fluidly connected to the lumen outlet of the corresponding end module, and the lumen outlet of the intermediate module being fluidly connected to the lumen inlet of the corresponding lead module.
15. The system of claim 13, further comprising a pH control subsystem configured to control pH of the acidic solution.
16. The system of claim 13, further comprising at least one flow control subsystem configured to control flow rate of the acidic solution and/or the source of the aqueous solution.
17. The system of claim 13, further comprising a temperature control subsystem configured to control temperature of the aqueous solution.
18. A method of treating an aqueous solution comprising ammonia with a system comprising a plurality of modules, each module comprising a plurality of membranes, each membrane having a lumen side and a shell side, the method comprising:
- directing the aqueous solution comprising ammonia to a shell inlet of a lead module to produce a first effluent, the first effluent being fluidly connected to a shell inlet of an end module,
 - directing an acidic solution to a lumen inlet of the end module, the ammonia being filtered through the plurality of membranes of the end module to produce a first intermediate product comprising ammonium and a second effluent,
 - the first intermediate product being fluidly connected to a lumen inlet of the lead module, the ammonia being filtered through the plurality of membranes of the lead module to produce a second intermediate product comprising ammonium.
19. The method of claim 18, further comprising directing the second intermediate product to a reservoir comprising an acid to produce the acidic solution.

20. The method of claim 19, further comprising controlling pH of the acidic solution by addition of an effective amount of the acid.

5 21. The method of claim 19, further comprising withdrawing a product comprising ammonium from the reservoir.

22. The method of claim 21, further comprising drying the product comprising ammonium to produce a fertilizer product.

10

23. The method of claim 18, further comprising directing the second effluent to a point of use.

24. The method of claim 18, further comprising controlling temperature of the aqueous
15 solution to be between 95°F and 150°F.

25. The method of claim 18, further comprising controlling flow rate of the aqueous solution and the acidic solution.

20