



(12) **DEMANDE DE BREVET CANADIEN**
CANADIAN PATENT APPLICATION

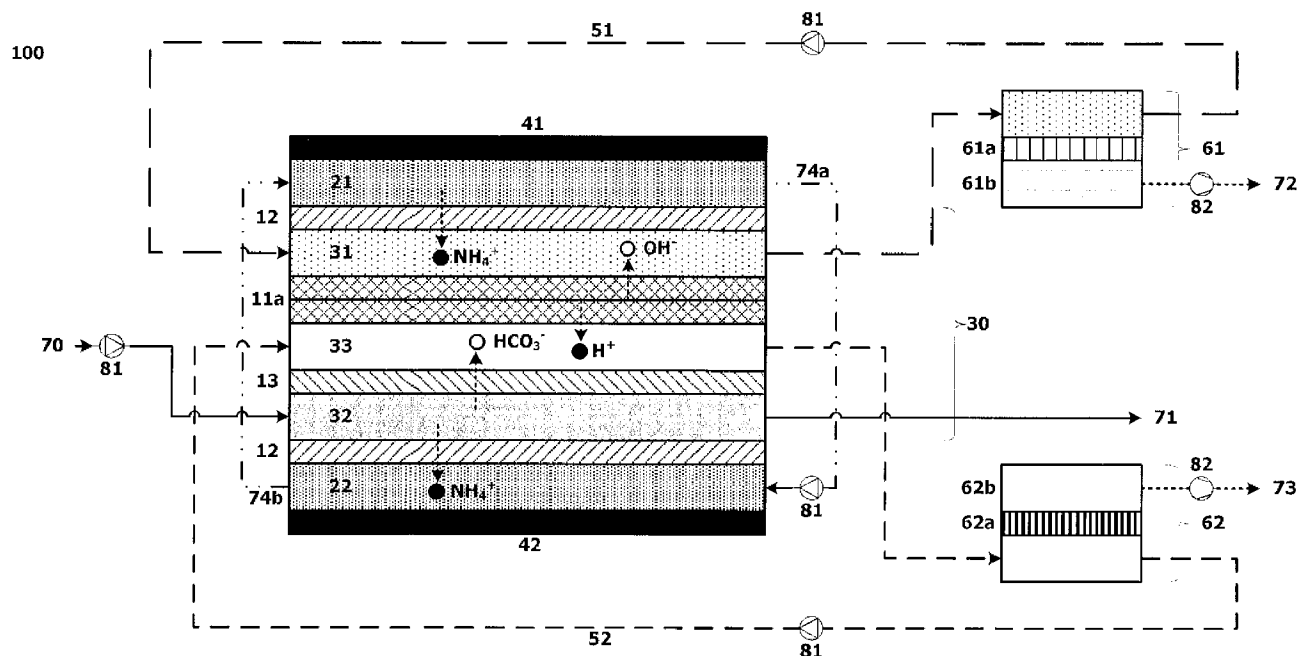
(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2019/01/31
(87) Date publication PCT/PCT Publication Date: 2019/08/08
(85) Entrée phase nationale/National Entry: 2020/08/04
(86) N° demande PCT/PCT Application No.: NL 2019/050058
(87) N° publication PCT/PCT Publication No.: 2019/151855
(30) Priorités/Priorities: 2018/02/01 (NL2020369);
2018/03/05 (NL2020528)

(51) Cl.Int./Int.Cl. *C02F 1/20* (2006.01),
B01D 19/00 (2006.01), *B01D 61/44* (2006.01),
B01D 61/58 (2006.01), *C02F 1/469* (2006.01)
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(54) Titre : RECUPERATION DE GAZ PROVENANT D'EAUX USEES
(54) Title: GAS RECOVERY FROM WASTEWATER

Fig. 1



(57) **Abrégé/Abstract:**

The present invention is in the field of a system for gas recovery from wastewater, a method for treating wastewater, and a method wherein ammonia and carbon dioxide are recovered. Typically a wastewater stream is fed into the system, treated and stripped from ammonia and carbon dioxide, and a cleaner stream is released.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

08 August 2019 (08.08.2019)



(10) International Publication Number

WO 2019/151855 A1

(51) International Patent Classification:

C02F 1/20 (2006.01) *B01D 61/44* (2006.01)*C02F 1/469* (2006.01) *B01D 61/58* (2006.01)*B01D 19/00* (2006.01) *C02F 101/16* (2006.01)

(21) International Application Number:

PCT/NL2019/050058

(22) International Filing Date:

31 January 2019 (31.01.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2020369 01 February 2018 (01.02.2018) NL

2020528 05 March 2018 (05.03.2018) NL

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: GAS RECOVERY FROM WASTEWATER

(57) Abstract: The present invention is in the field of a system for gas recovery from wastewater, a method for treating wastewater, and a method wherein ammonia and carbon dioxide are recovered. Typically a wastewater stream is fed into the system, treated and stripped from ammonia and carbon dioxide, and a cleaner stream is released.



WO 2019/151855 A1

WO 2019/151855 A1

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *with amended claims (Art. 19(1))*

Gas recovery from wastewater

FIELD OF THE INVENTION

The present invention is in the field of a system for gas recovery from wastewater, a method for treating wastewater, and a method wherein ammonia and carbon dioxide are recovered. Typically a wastewater stream is fed into the system, treated and stripped from ammonia and carbon dioxide, and a cleaner water stream is released.

BACKGROUND OF THE INVENTION

Typically wastewater originates from households and industry. It may be collected and transferred to a treatment facility.

Wastewater treatment is aimed at converting wastewater into an aqueous effluent that can be returned to the nature water cycle, or aimed at (direct) reuse of water. The latter is also referred to as water reclamation. A minimal impact on the environment is aimed at. The treatment process typically takes place in a wastewater treatment plant or sewage treatment plant. Typically pollutants are removed or broken down. Various processes may be involved, such as phase separation, sedimentation, filtration, oxidation, polishing, tertiary treatment, and biochemical treatment, such as by using microorganisms. By-products from wastewater treatment plants may also be treated in a wastewater treatment plant.

A contaminant typically found in wastewater is nitrogen, such as in the form of urea, nitrate and nitrite. Excessive discharge of nitrogen (N) leads to eutrophication of receiving surface waters and subsequent deterioration of the aquatic environment. To prevent this, nitrogen compounds in wastewaters are preferably removed before discharge of the water. In various types of wastewater, N is present as ammonium ion (NH_4^+) in combination with an ion such as bicarbonate (HCO_3^-). In many industrialized areas in the world, NH_4^+ is converted to nitrates and eventually to dinitrogen gas, at the expense of considerable capital costs and energy.

The majority of the produced NH_3 is used as fertilizer. As a consequence of use thereof, ultimately NH_3 becomes available in waste streams: for example, in manure, urine, and sewage. The total amount of NH_3 discharged to domestic sewage treatment

plants in 2016 in the Netherlands was about 32 million kilogram, while the amount of NH_3 in manure in 2013 was about 471 million kilograms. Current state-of-the-art technologies require at least 11 MJ/kg- NH_3 to remove NH_3 from wastewater.

5 A treatment technology used is Anammox. In wastewater containing NH_4HCO_3 , NH_4^+ is biochemically oxidized, forming N_2 and H_2O . This process requires ~~electrical~~ energy. The application of Anammox finally does not lead to the possibility of resource or energy recovery. Also CO_2 may remain in treated water,
10 ter, leading to amongst others acidification.

Ammonium nitrate may be removed from wastewater. However, in such as treatment of wastewater containing NH_4NO_3 species, the NH_4NO_3 can unfortunately not be reused in certain cases because it contains traces of radioactive compounds.

15 For $(\text{NH}_4)_2\text{SO}_4$ fertilizer production initially CO_2 may be stripped and released into the air to increase the pH and lower the buffer capacity. Subsequently, NH_3 gas is stripped, requiring significant amounts of energy and the addition of chemicals. The NH_3 is then scrubbed in acid, to produce
20 $(\text{NH}_4)_2\text{SO}_4$, which can be used as (resource for) fertilizer. However, the demand and economic yield of $(\text{NH}_4)_2\text{SO}_4$ are low: the required acid is more valuable per kg than the produced $(\text{NH}_4)_2\text{SO}_4$. Additionally, there are extra costs for the required chemicals and energy. Because this fertilizer has a high sulphur content, the applicability is limited to specific situations.
25

Some prior art documents relate to gas recovery from aqueous systems.

30 US 2016/271562 A1 recite a process and system for removing ammonia from an aqueous ammonia solution. A first aqueous solution and the ammonia solution are flowed respectively through a first and a second separation chamber of a bipolar membrane electrodialysis stack. The first separation chamber is bounded on an anodic side by a cation exchange membrane and
35 the second separation chamber is bounded on a cathodic side by the cation exchange membrane and on an anodic side by a bipolar membrane. The bipolar membrane has an anion-permeable layer and a cation-permeable layer respectively oriented to face the stack's anode and cathode. While the solutions are

flowing through the stack a voltage is applied across the stack that causes the bipolar membrane to dissociate water into protons and hydroxide ions. The protons migrate into the second separation chamber and react there with ammonia to form ammonium ions that migrate to the first separation chamber.

US 4,969,983 A recites an apparatus containing a multiplicity of three chamber units comprising a combination of ion exchange membranes and bipolar membranes with certain of said chambers containing a fluid permeable filler of ion-exchange material. The apparatus can be used in a process to remove weakly ionized gases from fluid mixtures.

An article by Pronk et al. "Treatment of source-separated urine by a combination of bipolar electrodialysis and a gas transfer membrane" in Water Science Technology, 53, 3, p. 139-146, 2006, recites that urine contains nutrients which can be applied usefully as a fertiliser in agriculture, but the relatively high pH can lead to ammonia evaporation. Electrodialysis with bipolar membranes was combined with an additional mass transfer unit in order to render a product containing ammonium and phosphate at a low pH. In one case, the additional mass transfer unit consisted of bubble columns placed in acid and basic concentrate streams, connected with a circulating gas phase. In the other case, the unit consisted of a gas-filled (hydrophobic) membrane placed in between the circulating acid and basic concentrate streams. The results showed that ammonia was transferred through the gas phase, but also carbonate, which is present in stored urine originating from the hydrolysis of urea. Although the pH in the product stream decreases initially, it rises above pH 7 at longer operation times. This pH increase can be attributed to a combination of proton compensating effects. The use of ammonia-selective membranes for the transfer into the acid concentrate could provide a solution to generate an ammonium phosphate product at low pH and high recoveries.

An article by Shuangchen et al. "Experimental study on desorption of simulated solution after ammonia carbon capture using bipolar membrane electrodialysis", Int. J. Greenhouse Gas Control, Elsevier, Vol. 42, November 3, 2015, p. 690-698, recites ammonia capture in solutions.

An article by Ali et al. in J. Membrane Science, Elsevier, Vol. 244, Nr. 1-2, November 15, 2004, p. 89-96 recites that splitting of ammonium nitrate to nitric acid and ammonia was achieved by a coupled process including bipolar membrane electro-
dialysis and in situ ammonia stripping. The effect of homo-
polar ion-exchange membranes on current efficiency led to the
selection of specific membranes. The main parameters influencing the current efficiency were acid and ammonia concentrations. Proton leakage through the anion-exchange membrane is
proportional to acid concentration. Ammonia diffuses through
the membranes independently of the current. Higher current efficiency was obtained at higher current density. Batch and
continuous processing were compared.

A further issue with prior art systems may be potential
fouling of the membranes used. Therefore one has to cope with
the various contaminants present in wastewater. As mentioned
the required energy, the process control strategy, and the
economic feasibility, is sub-optimal.

The present invention therefore relates to a system for gas
recovery from wastewater, and a method of operating such a
system, which solve one or more of the above problems and
drawbacks of the prior art, providing reliable results, without jeopardizing functionality and advantages.

SUMMARY OF THE INVENTION

The present invention relates to a system for gas recovery
from wastewater, a method for treating wastewater, and a
method wherein ammonia and carbon dioxide are recovered. The
present invention relates to an innovative process in which
wastewater with dissolved NH_4HCO_3 is treated with a combination
of two technologies: electrodialysis with bipolar membranes
and stripping of gases, such as with a vacuum membrane. By applying an electrical potential difference in electrodialysis
with bipolar membranes it has been found that NH_4^+ transfers
from the wastewater to an alkaline recirculation solution.
Simultaneously HCO_3^- is found to transfer from the wastewater
to an acidic recirculation solution, leading to the depletion
of NH_4HCO_3 in the wastewater. In addition to ion transfer
through ion exchange membranes, bipolar membranes dissociate
water into ions under the influence of an electrical potential

difference. This results in the generation of H^+ ions in the acidic recirculation solution, leading to the formation of dissolved carbon dioxide gas (CO_2). In the alkaline solution, OH^- is generated, leading to the formation of dissolved ammonia gas (NH_3). The two gases (CO_2 and NH_3) are subsequently stripped, such as by separate vacuum membrane removal. A hydrophobic membrane (impermeable for liquids, but permeable for gases) may separate the liquid phase from the gaseous phase (CO_2 and NH_3 , respectively). On the gaseous side of the membrane an under-pressure (vacuum) may be applied. Because of a vapour pressure difference, the gases are stripped from the liquid, resulting in recovery of CO_2 and NH_3 gas. These gases may be used to produce fertilizer, to produce energy (from NH_3), or to be applied directly as a resource in industry. The alkaline and acidic recirculation solutions are recycled in the electrodialysis with bipolar membranes. The present process is found to be very efficient in terms of energy used and in terms of product obtained.

The present combination of technologies enables separate recovery of resources (CO_2 gas and NH_3 gas) in treatment of wastewater comprising NH_4^+ and HCO_3^- . Additionally, the invention provides resource recovery in wastewater treatment without addition of chemicals in a continuously operated process. Only electrical energy is required, while additional low-grade energy (waste heat) can be used to improve the efficiency of the invention. Finally, the invention does not continuously generate a residual solution which needs to be treated further; CO_2 and NH_3 gas are potential end-products, whereas the treated water can be discharged or reused (optionally after post-treatment). The gases may be obtained in high purity, e.g. >90% pure. For both gaseous species, CO_2 and NH_3 , the other species is virtually absent; in both cases water vapour may be present. The present invention is sustainable, as it contributes to a circular economy, where water, NH_3 and CO_2 may be reused. It is also very scalable. Both electrodialysis and membrane stripping can be applied in a very wide range of wastewater quantities, e.g. because these technologies can be implemented in a modular way.

The present invention provides economical and material savings for e.g. domestic wastewater treatment and manure. It has been found that 10 MJ/kg-NH₃ can be recovered as electrical energy when using NH₃ as fuel for a solid oxide fuel cell. This amount of recovered energy can be partly used to remove NH₃ from wastewater. In this situation, the removal of NH₃ does not cost energy anymore, resulting in a saving of 0.25 euro/kg-NH₃, assuming that electricity costs 0.08 euro/kWh. This is a total potential saving of 126 million euro per year in the Netherlands only.

The production of NH₃ from N₂ and H₂ by the Haber-Bosch process requires 25 MJ/kg-NH₃ (theoretical minimum is 20 MJ/kg-NH₃). When NH₃ is recovered as a resource from wastewater and it can be reused 0.31 euro/kg-NH₃ can be saved, as the NH₃ does not have to be produced anymore. This is a total potential saving of 156 million euro per year in the Netherlands. For this situation, it is assumed that the amount of energy to recover NH₃ is equal to the current amount of energy for NH₃ removal from wastewater.

Some drawbacks exist however. At present there are relatively high costs for the membranes, some cleaning is still involved, and it is preferred, in view of transport, to have an application for the generated CO₂ close to the present system.

The present system comprises at least one ion exchange unit 30. Into the at least one exchange unit wastewater is provided through input 70, which is treated by the present system, and released from the system through output 71. In fluid connection with the at least one exchange unit are at least three recirculation units 51, 52, 74a, b, a first alkaline unit, a second acidic unit, and a third electrode rinse recirculation unit 74a, b adapted to receive input from a first electrode rinse compartment (21, 22), and for providing output to at least one of electrode rinse (21, 22), wherein at least one recirculation unit comprises a hydrophobic membrane (61a, 62a), a molecular sieve for ammonia or for CO₂, respectively, a pervaporation membrane, or a combination thereof, and at least one of a tube (72) for removing gaseous ammonia, and a tube (73) for removing gaseous CO₂. For providing flow of

fluids a pump, 81 respectively, is provided. Clearly these alkaline and acidic recirculation units are separate from one and another. In the alkaline recirculation unit NH_3 (ammonia) is stripped, whereas in the acidic recirculation unit CO_2 is stripped, both as gaseous species. The stripped gases may exit the present system over optional tubes 72,73, respectively. For stripping and flowing gases pumps 82 may be provided, which typically provide an under-pressure. The stripped gases may be combined to form NH_4HCO_3 . Each ion exchange unit comprises at least three compartments separated by membranes. The membranes provide exchange of NH_4^+ (ammonium) from the second to the first compartment over the cation exchange membrane 12, and of HCO_3^- from the second to the third compartment over the anion exchange membrane 13; hence the membranes may be referred to as ion exchange membranes, such as cation and anion exchange membranes. The present also comprises at least two electrode rinse compartment 21,22, and typically two electrode rinse compartments; the at least two electrode rinse compartment have an adjacent membrane, selected from bipolar membranes, cation exchange membranes, and anion exchange membranes, respectively, which may provide exchange of NH_4^+ , H^+ , OH^- , or HCO_3^- , to or from the electrode rinse compartment 21,22, respectively. The third recirculation unit replenishes the at least electrode rinse compartment. The at least one electrode rinse compartment 21 may be in electrical contact with an anode 42 and the at least one electrode rinse compartment 22 may be in electrical contact with a cathode 41. To the anode/cathode an electrical current is provided. Water and electrons form H^+ and OH^- . Typically the following redox reactions occur: Anode: $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$; Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$. If the electrode drain recirculates from compartment 21 to compartment 22, and vice versa, water is formed again. The bipolar membrane (11a,b) is typically facing the alkaline compartment 31 or electrode rinse compartment 22 with a positive side and mutatis mutandis is typically facing the acidic compartment 33 or electrode rinse compartment 21 with a negative side. The bipolar membranes can generate H^+ , at a negative side thereof, and OH^- , at a positive side thereof.

In a second aspect the present invention relates to a

method of treating wastewater, comprising NH_4^+ , and HCO_3^- , using the present system.

Thereby the present invention provides a solution to one or more of the above mentioned problems and drawbacks.

5 Advantages of the present description are detailed throughout the description.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates in a first aspect to a system according to claim 1.

10 In an exemplary embodiment of the present system the third recirculation unit 74a,b may be adapted to receive input from the first electrode rinse compartment 21, and for providing output to the second electrode rinse compartment 22, and vice versa. Therewith the liquids in the compartments may be
15 replenished. A salt level in the compartments 21,22 may be 0.1-2 mole/l, such as by providing Na_2SO_4 , NaNO_3 , NH_4NO_3 , or NH_4HCO_3 .

In an exemplary embodiment of the present system the first electrode rinse compartment 21 may comprise NH_4^+ or H^+ ,
20 or wherein the second electrode rinse compartment 22 comprises OH^- or HCO_3^- , or a combination thereof.

In an exemplary embodiment of the present system the at least one recirculation unit may comprise a membrane 61a, 62a, which typically is hydrophobic, such as a macroporous hydro-
25 phobic membrane, a molecular sieve for ammonia or for CO_2 , respectively, a pervaporation membrane, a pump 82, or a combination thereof.

In an exemplary embodiment of the present system at least one membrane 61a,62a in the stripper may be impermeable to
30 liquids, such as water, and permeable to gases, such as CO_2 and NH_3 , respectively. The stripper 61,62 typically comprises a strip chamber 61b,62b, respectively.

In an exemplary embodiment of the present system the (hydrophobic) membrane 61a, 62a may be macroporous, with an average pore size of 50-500 nm, or microporous, with an average
35 pore size of 0.4-10 nm, preferably 0.5-1 nm (as determined by electron microscopy).

In an exemplary embodiment of the present system the membrane 11a,11b,12,13,61,62 may have a size from 50 cm^2 to 10^4

cm², such as 10²-10³ cm², and a thickness of 100-7000 µm, such as 200-900 µm, a compartment 31,32,33,21,22 may have a width of 0.1-50 mm, such as 1-30 mm, and a flow may be parallel to the membrane. A membrane may comprise a support. Membranes 12
5 may be polyvinyl chloride based, with sulphonic acid in Na⁺ ionic form, membranes 13 may be polyester based, with ammonium in Cl⁻ ionic form.

In an exemplary embodiment of the present system the membrane 61a,62a, may be selected from polymeric material, preferably thermoplastic polymers, such as poly propylene and poly
10 vinylidene fluoride, inorganic material, such as silica, and reinforced silica, and combinations thereof.

In an exemplary embodiment of the present system the exchange unit 30 may comprise a stack of a cation exchange membrane 12, an alkaline compartment 31, a bipolar membrane 11a,
15 an acidic compartment 33, an anion exchange membrane 13, and a wastewater compartment 32, and wherein the second electrode rinse compartment 22 is in fluidic contact with a further cation exchange membrane 12, and wherein the third recirculation
20 unit 74a,b is adapted to receive input from a first electrode rinse compartment 22 to compartment 21, and adapted to provide output to compartment 22 (see fig. 1,2). Therein a cathode 42 may be provided in contact with a compartment 22 and an anode 41 may be provided in contact with compartment 21.

In an exemplary embodiment of the present system the exchange unit 30 may comprise a stack of an anion exchange membrane 13, an acidic compartment 33, a bipolar membrane 11a, an
25 alkaline compartment 31, a cation exchange membrane 12, and a wastewater compartment 32, and wherein the second electrode rinse compartment 22 is in fluidic contact with a further anion exchange membrane 13, and wherein the third recirculation
30 unit 74a,b is adapted to receive input from a first electrode rinse compartment 21 to compartment 22, and adapted to provide output to compartment 21. Therein a cathode 42 may be provided
35 in contact with a compartment 21 and an anode 41 may be provided in contact with compartment 22.

In an exemplary embodiment of the present system the exchange unit 30 may comprise a stack of an bipolar membrane 11a, an alkaline compartment 31, a cation exchange membrane

12, a wastewater compartment 32, an anion exchange membrane 13, and an acidic compartment 33, and wherein the second electrode rinse compartment 22 is in fluidic contact with a further bipolar membrane 11b, and wherein the third recirculation unit 74a,b is adapted to receive input from a first electrode rinse compartment 21 to compartment 22, and adapted to provide output to compartment 21, and vice versa to compartment 22 (see fig. 3). Therein a cathode 42 may be provided in contact with a compartment 21 and an anode 41 may be provided in contact with compartment 22.

In an exemplary embodiment the present system may comprise 2-2¹⁰ ion exchange units 30 in parallel, preferably 4-2⁹ ion exchange units, such as 200-400 ion exchange units.

In an exemplary embodiment the present system may comprise at least one of a tube 72 for removing gaseous ammonia, and a tube 73 for removing gaseous CO₂.

In an exemplary embodiment of the present system in operation at least one of a voltage of 0.1-5 V per ion exchange unit 30 may be applied, preferably 0.3- 3V, more preferably 0.5- 2V, such as 0.7-1.5V.

In an exemplary embodiment of the present system in operation a pH in the first alkaline compartment 31 may be from 7-14, preferably from 8-13, such as 9-12.

In an exemplary embodiment of the present system in operation a pH in the third acidic compartment 33 may be from 1-7, preferably 2-6.5, such as 2-6.

In an exemplary embodiment of the present system in operation a current density may be from 15-500 A/m², such as 50-100 A/m².

In an exemplary embodiment of the present system in operation a flow parallel to a membrane may each individually be from 0.01-0.20 m/s, such as 0.05-0.10 m/s.

In an exemplary embodiment of the present system in operation a NH₄⁺ flux over a membrane may each individually be 0.2-20 mole/m²/h, preferably 0.5-5 mole/m²/h, such as 1-2 mole/m²/h.

In an exemplary embodiment of the present system in operation a HCO₃⁻ flux over a membrane may each individually be 0.2-20 mole/m²/h, preferably 0.5-5 mole/m²/h, such as 1-2

mole/m²/h.

In an exemplary embodiment of the present system in operation an operating temperature may be from 10-80 °C.

5 In an exemplary embodiment of the present system in operation the [NH₄⁺] and [HCO₃⁻] in the second compartment 32 may each individually be 10⁻³-2 mole/l, preferably 10⁻²-1 mole/l, such as 10⁻¹-0.5 mole/l.

10 In an exemplary embodiment of the present system in operation an NH₃ flux and a CO₂ flux in recirculation units 51,52 may each individually be 50-5000 g/m²/h, preferably 70-2500 g/m²/h, such as 100-1000 g/m²/h.

In an exemplary embodiment of the present system membranes 11a,b,12 and 13 are separated by spacers 2 and the membranes 11a,b,12 and electrodes are also separated by spacers.

15 In an exemplary embodiment of the present method transferring NH₄⁺ from the wastewater 70 to an alkaline recirculation solution 51 may be through a first compartment 31.

20 In an exemplary embodiment of the present method transferring HCO₃⁻ from the wastewater to an acidic recirculation solution 52 may be through a third compartment 33.

In an exemplary embodiment of the present method NH₄⁺ may be converted into NH₃ in the presence of OH⁻ in the first compartment 31, and wherein HCO₃⁻ may be converted into CO₂ in the presence of H⁺ in the third compartment 33.

25 In an exemplary embodiment of the present method NH₃ may be stripped in ammonia stripper 61, and wherein CO₂ may be stripped in CO₂ stripper 62.

30 In an exemplary embodiment of the present method at a gaseous side of stripper 61,62 an under pressure may be applied, such as of 0.1-90 kPa, preferably 1.5-75 kPa, such as 5-50 kPa.

In an exemplary embodiment the present method may comprise forming NH₄HCO₃.

35 In an exemplary embodiment of the present method wastewater may be provided by at least one of a domestic sewage treatment plant, a manure treatment facility, a fertilizer production plant, food and beverage industry, and an industry producing nitrogen loaded wastewater.

In the present method an electrical potential difference

over the cathode 42/anode 41 in electrodialysis with bipolar membranes 11a,11b is applied. Therewith decomposition of water is established. The wastewater fed into the second compartment of the at least one exchange unit. NH_4^+ is transferred from the wastewater 70 to an alkaline recirculation solution 51, and simultaneously, HCO_3^- is transferred from the wastewater to an acidic recirculation solution 52, over the respective membranes. NH_4HCO_3 is depleted in the wastewater, typically in a continuous or semi-continuous mode. However the present system may also be operated batch wise. Water is split over bipolar membranes 11a,11b thereby providing H^+ to the third compartment 33 and alkaline recycling compartment 21, respectively, and thereby providing OH^- to the first compartment 31 and acidic recycling compartment 22, respectively.

The one or more of the above examples and embodiments may be combined, falling within the scope of the invention.

EXAMPLES

The below relates to examples, which are not limiting in nature.

In experiments, $1.6 \cdot 10^{-5}$ kg of NH_4HCO_3 was removed from 1 litre synthetic wastewater, equalling 87% of the total NH_4HCO_3 initially present. In total, $3.6 \cdot 10^{-5}$ MJ of electrical energy was used to transfer the ions and generate OH^- and H^+ . This required 2.3 MJ/kg- NH_3 for NH_3 production in the alkaline solution and 5.9 MJ/kg- CO_2 production in the acidic solution. This includes the pumping energy consumption, accounting for 10% of the total energy consumption. Also, NH_3 was stripped from alkaline synthetic solution with various initial NH_3 concentrations (1.2, 8.5 and 13 g- NH_3 /L, respectively) at room temperature by vacuum membrane stripping. This resulted in fluxes of 0.10, 0.59 and 0.73 kg/ m^2 /h, respectively. The permeate content of NH_3 was 1.2%, 7.9% and 11.5%, respectively. The rest of the permeate was water vapour, making it possible to reuse the NH_3 .

The invention is further detailed by the accompanying figures, which are exemplary and explanatory of nature and are not limiting the scope of the invention. To the person skilled in the art it may be clear that many variants, being obvious

or not, may be conceivable falling within the scope of protection, defined by the present claims.

FIGURES

The invention although described in detailed explanatory
5 context may be best understood in conjunction with the accompanying figures.

Fig. 1-5 show schematics of the present system.

DETAILED DESCRIPTION OF THE FIGURES

In the figures:

- 10 100 present system
- 2 spacer
- 11 bipolar membrane
- 11a first bipolar membrane
- 11b second bipolar membrane
- 15 12 cation exchange membrane
- 13 anion exchange membrane
- 21 electrode rinse compartment (anodic)
- 22 electrode rinse compartment (cathodic)
- 30 ion exchange unit
- 20 31 first alkaline compartment
- 32 second salt compartment
- 33 third acidic compartment
- 41 anode
- 42 cathode
- 25 51 alkaline recirculation unit
- 52 acidic recirculation unit
- 61 ammonia stripper
- 61a (hydrophobic) membrane
- 61b strip chamber
- 30 62 gaseous CO₂ stripper
- 62a (hydrophobic) membrane
- 62b strip chamber
- 70 wastewater input
- 71 treated water output
- 35 72 tube for removing gaseous ammonia
- 73 tube for removing gaseous CO₂
- 74a electrode rinse recirculation unit
- 74b electrode rinse recirculation unit
- 81 liquid pump

82 vacuum pump

Fig. 1-3 show an exemplary set-ups of the present system.

Fig. 4 shows a stacked variant of the present system.

Fig. 5 shows optional spacers.

5 The figures have been detailed throughout the description.

Fig. 1 shows a cell triplet provided with cation exchange membranes at the electrodes.

Fig. 2 shows a cell triplet provided with anion exchange membranes at the electrodes.

10 Fig. 3 shows a cell triplet provided with bipolar membranes at the electrodes.

Fig. 4 represents a plural version of fig. 1.

Fig. 5 shows that all membranes (11,12 and 13) are separated by spacers 2. The spacers are made of polyethylene/silicone material and woven into a mesh. The liquids flow through
15 the void fraction of the spacers, forming the salt, acid and alkaline chambers. The spacers are sealed on the top and bottom, making sure that the liquids are not leaking out of the membrane stack. The electrodes (anode and cathode) and the
20 membranes next to the electrodes are also separated by spacers, forming the electrode rinse chambers.

AMENDED CLAIMS
received by the International Bureau on 03 June 2019 (03.06.2019)

1. Wastewater gas recovery system (100) for recovering NH_3 and CO_2 comprising

at least one ion exchange unit (30), each exchange unit comprising at least three ion exchange compartments (31,32,33),
5 each ion exchange compartment being in contact over a membrane with at least one adjacent compartment,

a first alkaline ion exchange compartment (31) being in fluidic contact with a positive side of first bipolar membrane (11a) and with a cation exchange membrane (12) and comprising aqueous NH_4^+ and OH^- ,
10

a second ion exchange compartment (32) being in fluidic contact with an anion exchange membrane (13) and with a cation exchange membrane (12) and comprising water, NH_4^+ , and HCO_3^- , and

15 a third acidic ion exchange compartment (33) being in fluidic contact with a negative side of a bipolar membrane (11b) and with an anion exchange membrane (13) and comprising aqueous H^+ and HCO_3^- ,

a wastewater input (70) for providing wastewater to the second compartment,
20

a treated water output (71) adapted to receive output from the second compartment,

a cathode (42) and an anode (41) for providing a voltage,

at least two electrode rinse compartments (21,22) being in electrical contact with the cathode (42) or with the anode (41) and with a membrane (11a,b,12,13), and comprising salt,
25

at least three recirculation units (51,52,74a,74b), including a first alkaline recirculation unit (51) adapted to receive input from the first alkaline compartment (31), comprising a pump (81), an gaseous ammonia stripper (61), and for providing stripped output to the first alkaline compartment (31), a second acidic recirculation unit (52) adapted to receive input from the third acidic compartment (33), comprising a pump (82), a gaseous CO_2 stripper (62), and for providing stripped output to the third
30 acidic compartment (33), and a third recirculation unit (74a,74b) adapted to receive input from a first electrode rinse compartment (21,22), and for providing output to at least one of
35

electrode rinse compartments (21,22), wherein ~~at least one~~ re-circulation unit (51) is in fluidic contact with a hydrophobic membrane (61a), a molecular sieve for ammonia, a pervaporation membrane, or a combination thereof, and/or wherein recirculation
5 unit (52) is in fluidic contact with a hydrophobic membrane (62a), a molecular sieve for CO₂, a pervaporation membrane, or a combination thereof, wherein the third recirculation unit (74a,b) is adapted to receive input from the first electrode rinse compartment (21), and for providing output to the second
10 electrode rinse compartment (22), and vice versa, and

a tube (72) for removing gaseous ammonia, and/or a tube (73) for removing gaseous CO₂.

2. System according to any of claims 1, wherein at least one membrane (61a,62a) in the stripper is impermeable to liquids,
15 and permeable to gases.

3. System according to any of claims 1-2, wherein the hydrophobic membrane (61a,62a) is macroporous, with an average pore size of 50-500 nm, or microporous, with an average pore size of 0.4-10 nm (as determined by electron microscopy).

20 4. System according to any of claims 1-3, wherein the membrane (61a,62a) is selected from polymeric material, inorganic material, and combinations thereof.

5. System according to any of claims 1-4, wherein the exchange unit (30) comprises a stack of a cation exchange membrane (12), an alkaline ion exchange compartment (31),
25 a bipolar membrane (11a), an acidic ion exchange compartment (33), an anion exchange membrane (13), and a wastewater ion exchange compartment (32), and wherein the second electrode rinse compartment (22) is in fluidic contact with a further cation exchange membrane (12), or
30

wherein the exchange unit (30) comprises a stack of an anion exchange membrane (13), an acidic ion exchange compartment (33), a bipolar membrane (11a), an alkaline ion exchange compartment (31), a cation exchange membrane (12), and a wastewater ion exchange compartment (32), and wherein the second electrode rinse
35 compartment (22) is in fluidic contact with a further anion exchange membrane (13), or

wherein the exchange unit (30) comprises a stack of an bipolar membrane (11a), an alkaline ion exchange compartment (31), a

cation exchange membrane (12), a wastewater ion exchange compartment (32), an anion exchange membrane (13), and an acidic ion exchange compartment (33), and wherein the second electrode rinse compartment (22) is in fluidic contact with a further bipolar membrane (11b).

6. System according to any of claims 1-5, comprising 2-2¹⁰ ion exchange units (30) in parallel.

7. System according to any of claims 1-6, wherein membranes (11a,b,12 and 13) are separated by spacers (2) and the membranes (11a,b,12) and electrodes are separated by spacers (2).

8. System according to any of claims 1-7, wherein in operation at least one of a voltage of 0.1-5 V per ion exchange unit (30) is applied,

a pH in the first alkaline ion exchange compartment (31) is from 7-14,

a pH in the third acidic ion exchange compartment (33) is from 1-7,

a current density is from 5-500 A/m²,

a flow parallel to a membrane is each individually from 0.01-0.20 m/s,

a NH₄⁺ flux over a membrane is each individually 0.2-20 mole/m²/h,

a HCO₃⁻ flux over a membrane is each individually 0.2-20 mole/m²/h,

an operating temperature is from 10-80 °C,

the [NH₄⁺] and [HCO₃⁻] in the second ion exchange compartment (32) is each individually 10⁻³-2 mole/l,

a vacuum of 0.1-90 kPa is each individually applied over membranes (61,62),

a flux of wastewater and recirculation is each individually 0.01-10 kg/m²/h, and

an NH₃ flux and a CO₂ flux in recirculation units (51,52) is each individually 50-5000 g/m²/h.

9. Method for treating wastewater comprising

providing a system (100) according to any of claims 1-8,

applying an electrical potential difference over the anode (41)/cathode (42),

providing wastewater in second ion exchange compartment (32) comprising NH₄⁺, and HCO₃⁻,

transferring NH_4^+ from the wastewater (70) to an alkaline recirculation solution (51),
simultaneously, transferring HCO_3^- from the wastewater to an
acidic recirculation solution (52),

5 depleting NH_4HCO_3 in the wastewater, and
splitting water over bipolar membranes (11a, 11b) thereby providing H^+ to the third acidic ion exchange compartment (33) and
thereby providing OH^- to the first alkaline ion exchange compartment (31),

10 wherein transferring NH_4^+ from the wastewater (70) to an alkaline recirculation solution (51) is through a first alkaline ion exchange compartment (31),

wherein transferring HCO_3^- from the wastewater to an acidic recirculation solution (52) is through a third acidic ion exchange
15 compartment (33),

wherein NH_4^+ is converted into NH_3 in the presence of OH^- in the first alkaline compartment (31), and wherein HCO_3^- is converted
into CO_2 in the presence of H^+ in the third acidic ion exchange compartment (33),

20 wherein NH_3 is stripped in ammonia stripper (61), and wherein CO_2 is stripped in CO_2 stripper (62).

10. Method according to any of claims 9, wherein at a gaseous side of stripper (61, 62) an under pressure is applied.

11. Method according to any of claims 9-10, further comprising forming NH_4HCO_3 .

12. Method according to any of claims 9-11, wherein
wastewater is provided by at least one of a domestic sewage
treatment plant, a manure treatment facility, a fertilizer production plant, food and beverage industry, and an industry producing
30 nitrogen loaded wastewater.

Fig. 1

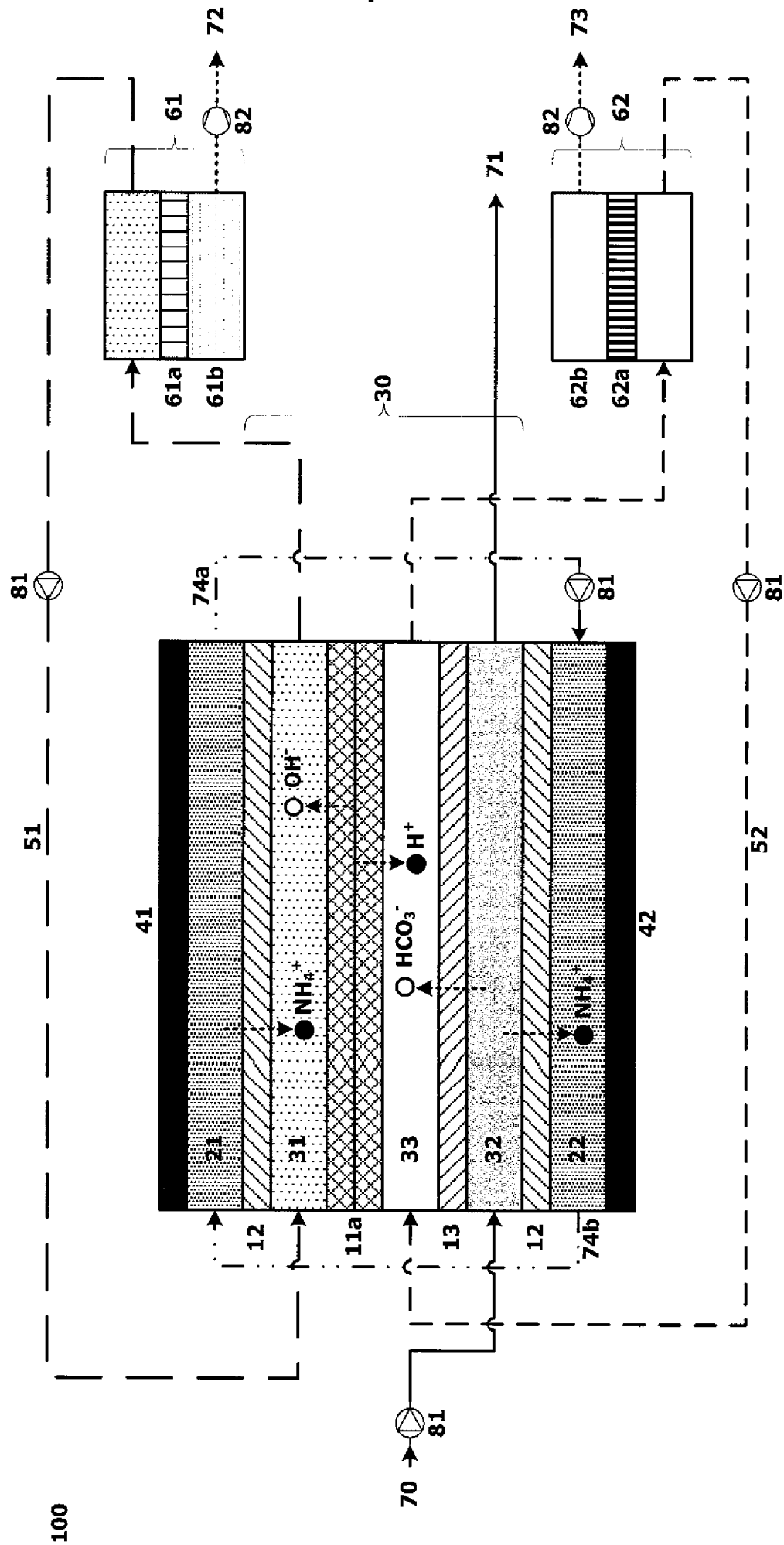


Fig. 2

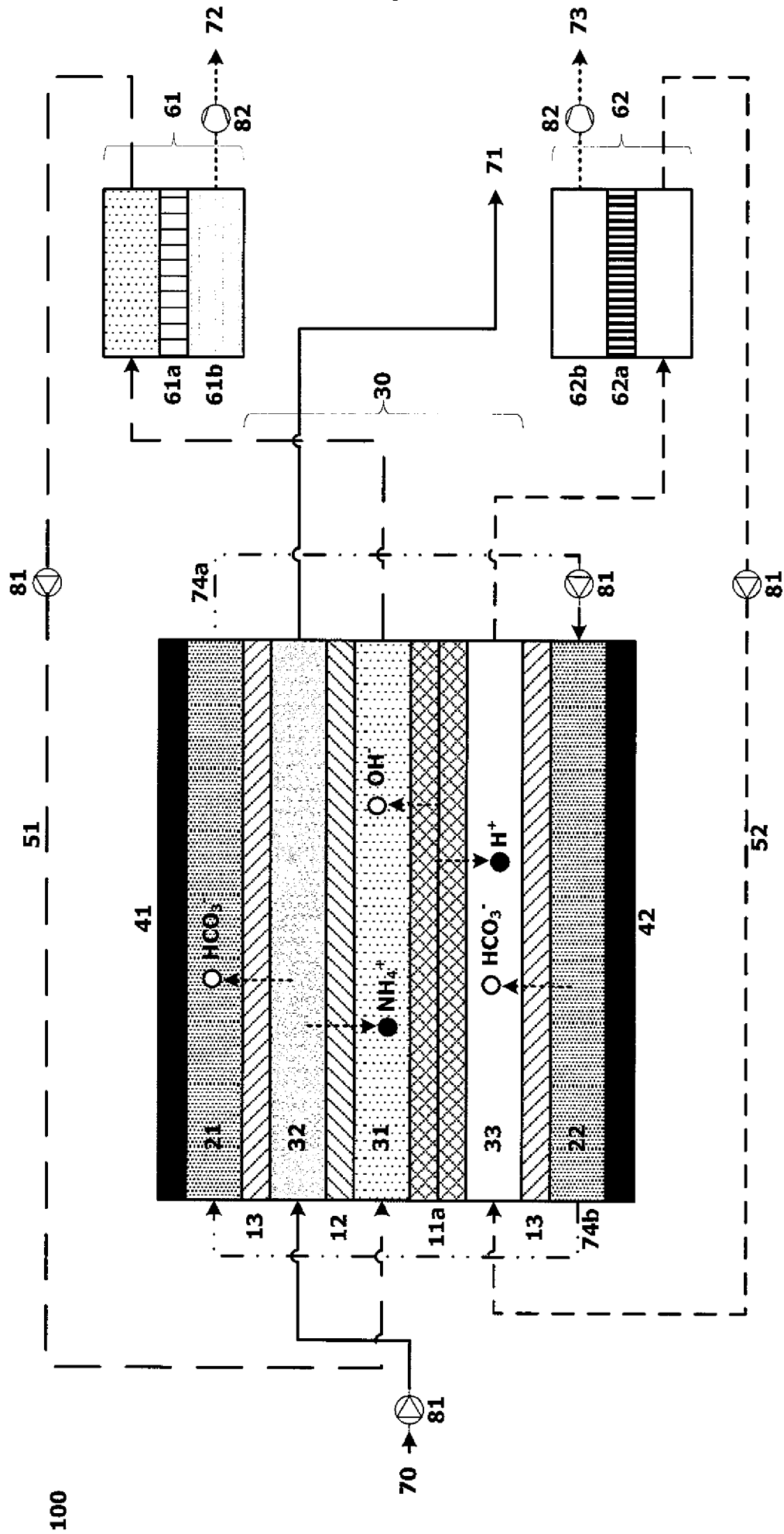


Fig. 3

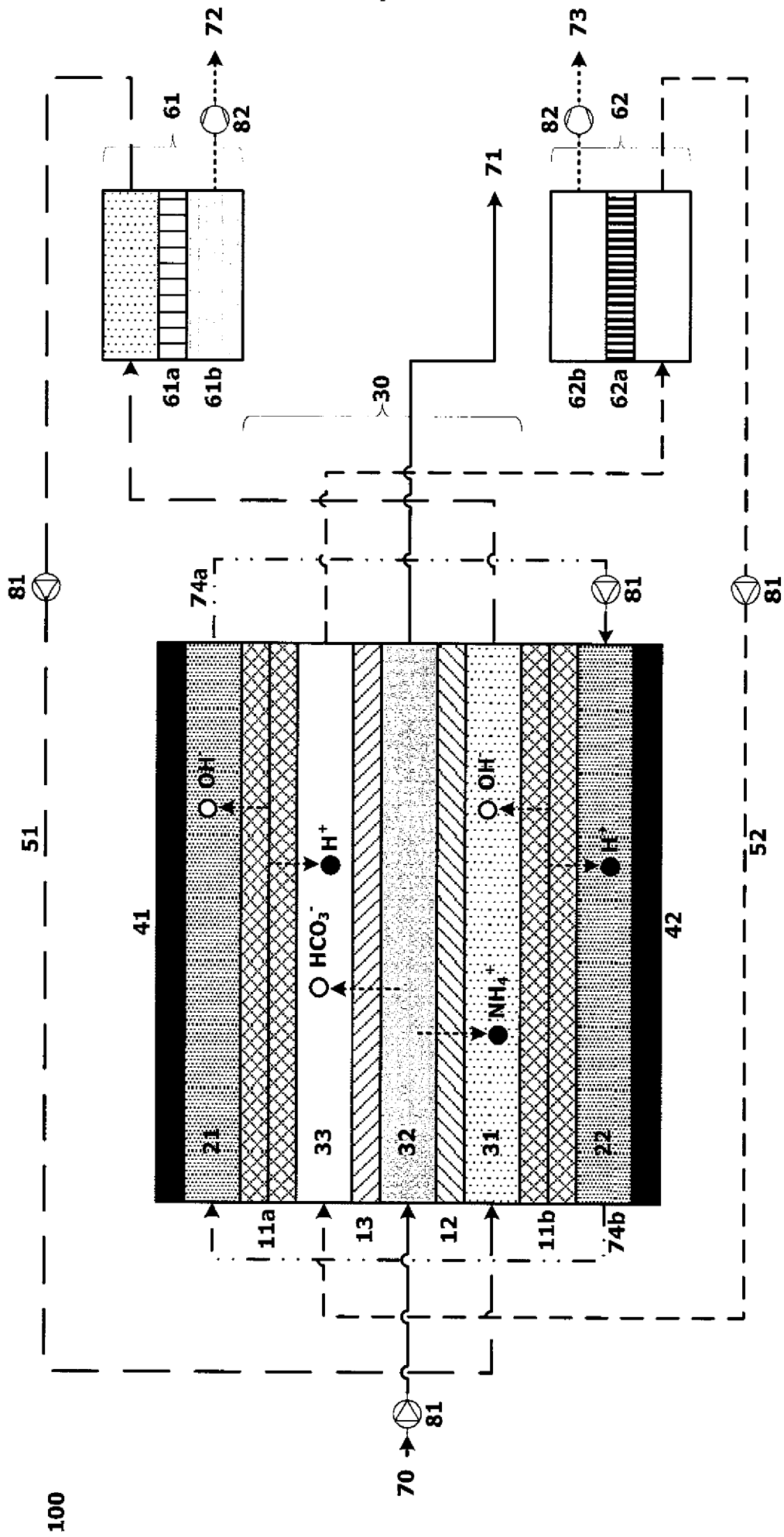
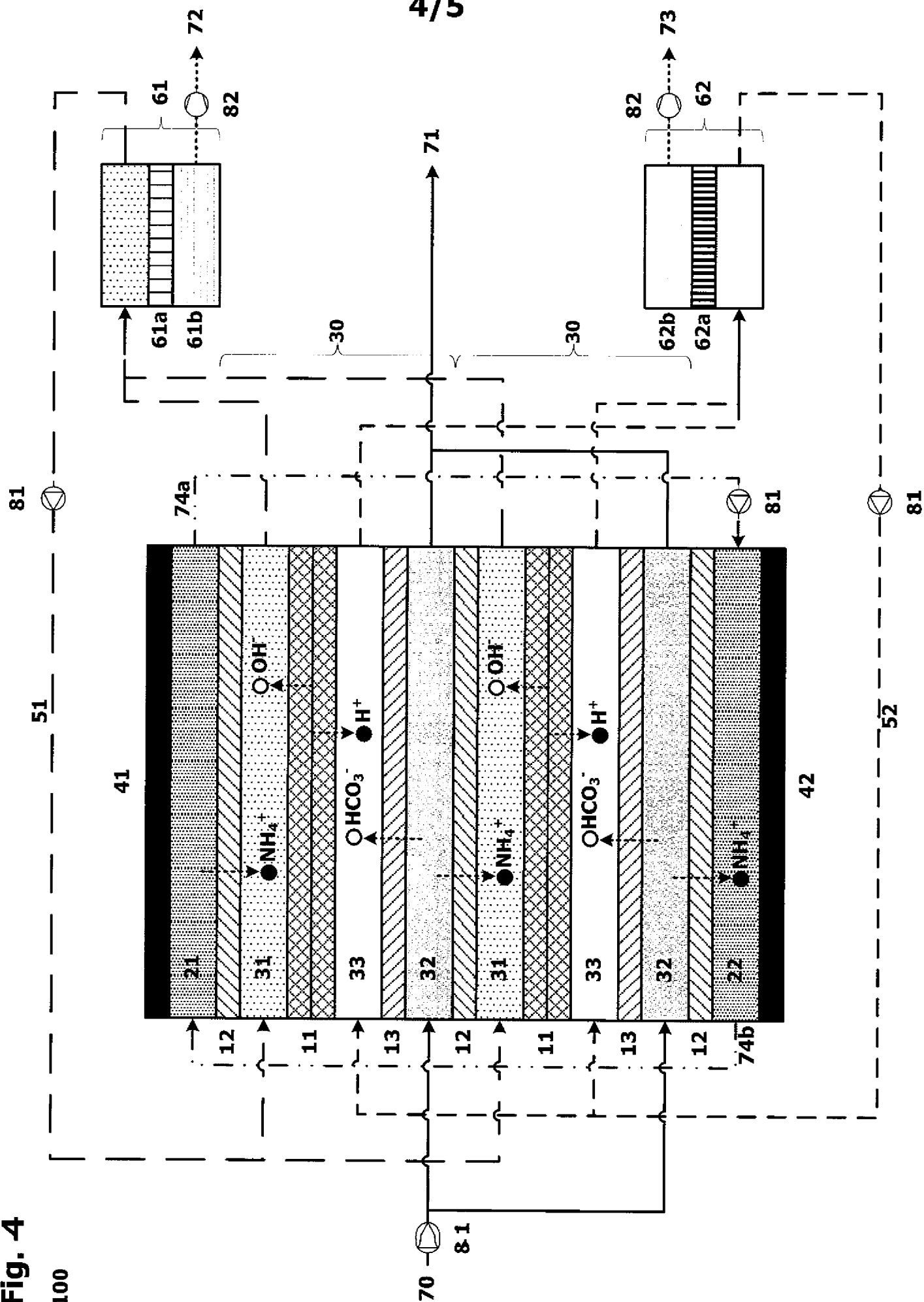


Fig. 4

100



5/5

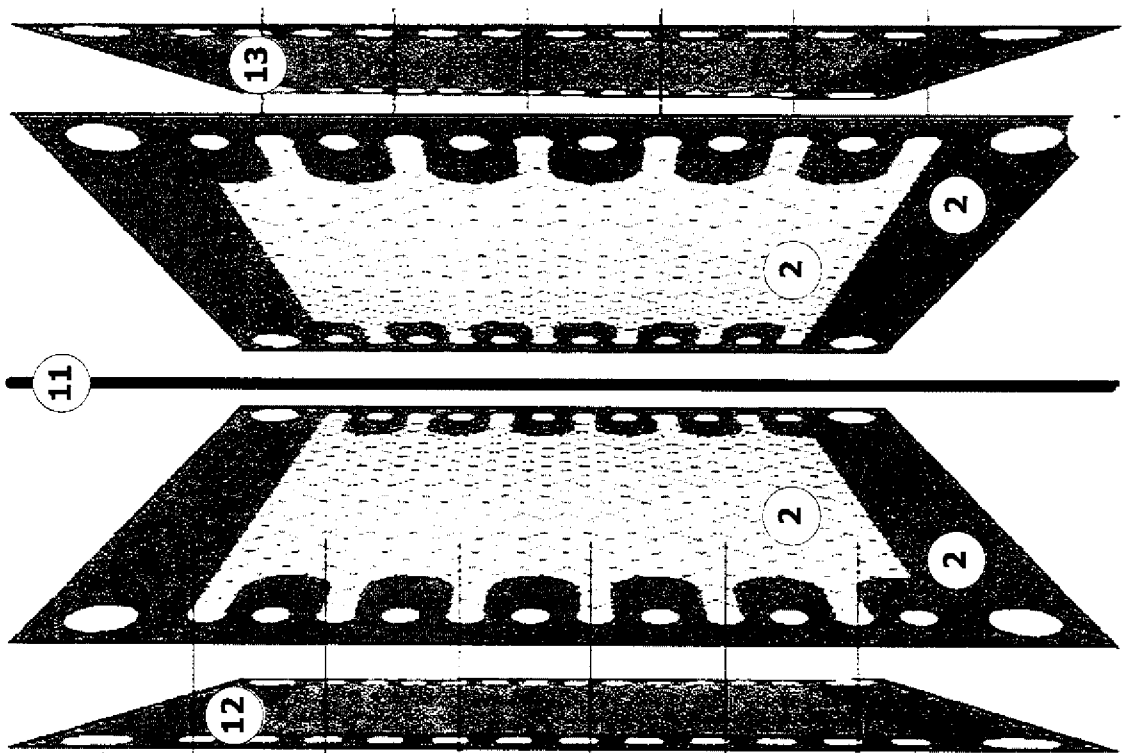


Fig. 5