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Nitrogen recovery from wastewater and human urine with hydrophobic gas separation membrane: experiments and modelling

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Abstract
In agriculture, the human urine could have been used as a natural fertilizer, although there are some problems with the direct utilization, such as the presence of micropollutants in urine, odour and storage of large volume of urine. Therefore, nutrients, such as nitrogen, can be recovered from urine. Continuous flow laboratory membrane reactor was built to investigate nitrogen recovery from wastewater and from human urine. Membrane gas separation method has not been investigated for ammonia recovery from human urine yet. Nitrogen as ammonia gas was recovered in acid using Zeus Aeos™ ePTFE gas-permeable hydrophobic membrane. Acid flux, operating pH, hydraulic retention time and effective membrane surface were experimentally determined. The aim of this work was to verify wastewater experiments in professional flowsheet environment, rigorously modelled with ChemCAD and optimized by dynamic programming optimization method: the membrane separation. Such nitrogen recovery membrane separation has not been published in this professional flowsheet environment yet. The objective function of the process is the ammonia harvesting efficiency. Eighty-five percentage ammonia harvesting efficiency can be reached with 60 membrane surface area/reactor volume ratio, at 35 °C feed temperature with 350 L/m²h acid and in 8 h' hydraulic retention time. It can be stated that this separation method is based on physical phenomena without any biological factors. The focus for nitrogen treatment in a wastewater treatment plant is removal instead of recovery. It can be determined that this system is capable for the nitrogen recovery from wastewater, and it can reduce the ammonia content of human urine too.

Keywords Human urine · Membrane technology · Nitrogen recovery · Gas-permeable hydrophobic membrane · Membrane modelling

Chemical terms
- CaCO3: Calcium carbonate
- Ca(OH)2: Calcium hydroxide
- H2SO4: Sulphuric acid
- Mg2+: Magnesium ion
- MgNH4PO4·6H2O: Magnesium ammonium phosphate hexahydrate
- MgO: Magnesium oxide
- N2: Nitrogen gas
- NaOH: Sodium hydroxide
- NH3: Ammonia
- NH4+: Ammonium ion
- (NH4)2SO4: Ammonium sulphate
- PO43−: Phosphate ion

Abbreviations
- AGMD: Air-gap membrane distillation
- BOD: Biochemical oxygen demand
Introduction

The nitrogen is the most significant nutrient for plants; and due to lack of nitrogen, the vegetative organs are developing poorly, the inflorescence will become scant and the yields decrease (Hajós 2005). The group of the solid-phased nitrogen fertilizers (Loch and Nosticzius 2004):

- ammonium salts,
- metal nitrates,
- and amid nitrogen content fertilizers.

Liquid fertilizers can be made also, from these listed fertilizers. In the group of ammonium (NH$_4^+$) salts, ammonium nitrate (the pure ammonium nitrate theoretical nitrogen content is 35%), calcium ammonium nitrate (CAN, the mix of ammonium nitrate and CaCO$_3$ dust) and ammonium sulphate nitrate (nitrogen content is at least 26%) has to be mentioned. Natrium-nitrate (nitrogen content is 16%) and calcium-nitrate (15.5–18% nitrogen content) belong to the group of metallic nitrates. The other group of nitrogen fertilizers urea, liquid ammonia (NH$_3$), aqueous ammonia, urea ammonium nitrate solution (UAN) has to be mentioned (Loch and Nosticzius 2004).

Instead of nitrogen-based fertilizers, human urine can be used as a natural fertilizer. Utilizing human urine in the agriculture still can be problematic because of several reasons.

To avoid the problems in connection with the direct and inappropriate application of human urine, there is a demand for a concentrated fertilizing product in crystalline form, such as NH$_4$NO$_3$, struvite or ammonium sulphate. Several processes (e.g. evaporation, freeze–thaw and reverse osmosis) have been considered in finding an effective method to reduce the water content of human urine. Significant water reduction was achieved by evaporation (> 96%) and the freeze–thaw process (75%), although these processes required unacceptably intensive energy. Furthermore, the dissolved ammonia contained in source-separated human urine can be easily evaporated to the atmosphere during the process (Tun et al. 2016).

The significant part of research papers related to using human urine as a fertilizer is concerned with the direct use of urine on agricultural fields reporting plant growth (Beler-Baykal et al. 2011).

Many technologies can recover nutrients through struvite precipitation (Antonini et al. 2011; Etter et al. 2011; Ganrot et al. 2007; Ronteltap et al. 2010), adsorption (Lind et al. 2000), ammonia stripping (Antonini et al. 2011; Başakçilardan-Kabakci et al. 2007; Liu et al. 2015), the combination of air stripping and absorption (Başakçilardan-Kabakci et al. 2007), membrane distillation and membrane gas separation.

The aim of this study is to summarize the referred technologies and to investigate hydrophobic gas separation membrane for nitrogen recovery from wastewater (as Sample I) and human urine (as Sample II). Laboratory experiments have to be carried out in order to model this membrane separation in professional flowsheet environment.

1. Struvite precipitation

The technology which recovers phosphate and nitrogen as struvite is based on a single-chamber microbial electrolysis cell (Cusick and Logan 2012), but controlled struvite recovery from wastewater or from human urine can be achieved with chemical reaction too. Crystal precipitation occurs when concentrations of Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$ exceed the solubility limit for struvite formation. As urine contains phosphate (PO$_4^{3-}$) and ammonium (NH$_4^+$), if magnesium is added to the urine, then the phosphate, ammonium and magnesium react and form crystalline struvite. This crystal can be filtered, collected and turned into fine powder (Etter 2009).

The struvite crystals are formed according to Eq. (1) equation in alkaline conditions (Zhang et al. 2009):

$$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \downarrow$$

(1)

Due to the production of struvite, 90% of phosphorus can be recovered from human urine (Etter 2009). An example of a small-scale process suitable, for example, for rural areas is described in (Rose et al. 2015). Production takes place in a stirred reactor and below the reactor valve, and a filter bag hangs to collect the struvite (Etter 2009; Rose et al. 2015; Tilley et al. 2009). Table 1 summarizes the advantages and disadvantages of struvite precipitation.

2. Nitrogen removal by combination of air stripping and absorption
Nitrogen can be recovered from human urine by the combination of air stripping and absorption (Başakçilardan-Kabakci et al. 2007; Antonini et al. 2011). There is a two-step chemical–physical process in precipitation reactor followed by stripping and absorption column. The method can generate magnesium ammonium phosphate (MAP or struvite, solid form) and ammonium sulphate \[(\text{NH}_4\text{)}_2\text{SO}_4, \text{liquid form}\]. These two products can be reused as fertilizers. In the precipitation reactor, MgO is dosed to stored urine in order to initiate struvite precipitation. In the second column, the air comes in contact with a sulphuric acid solution, which absorbed the ammonia from the gas phase in order to produce a liquid fertilizer in the form of ammonium sulphate (Antonini et al. 2011; Başakçilardan-Kabakci et al. 2007). Table 2 summarizes the advantages and disadvantages of stripping and absorption methods.

### Table 1  Pros and cons of the struvite precipitation (Etter 2009; Huang et al. 2016; Le Corre et al. 2005)

| Struvite precipitation |   |
|------------------------|--|
| **Pros**               | **Cons**                               |
| Phosphorus and nitrogen can be recovered simultaneously | Magnesium has to be in soluble form in sufficient quantity and at affordable price to operate a profitable struvite producer plant |
| As struvite also precipitates naturally from urine, any precipitate in the collection system should be incorporated into the final product, in order to maximize the nutrient recovery | As the solubility of struvite is low (0.033 g/100 ml in weakly acidic water), its leaching from soil is limited |
| It releases nutrients slowly, which can be favourable in the agriculture | |
| The application of human urine has to face with low social acceptance, but the odourless struvite product made of human urine usually has a good acceptance among farmers | |

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### 3. Membrane distillation

Membrane distillation (MD) is one of the promising techniques to recover nutrients from human urine, as it only requires low-grade heat (e.g. solar energy) to transfer volatile substances through a hydrophobic membrane by establishing a vapour pressure gradient (Dereese and Verliefde 2016). It can be mentioned that the direct-contact membrane distillation (DCMD) is the simplest structure capable of producing reasonable high flux and also the most tested MD configuration (Alkhudhiri et al. 2012; Derese and Verliefde 2016; Tun et al. 2016).

High ammonia concentration and alkaline condition of source-separated human urine lead to high volatile free ammonia (FA) content and consequent significant ammonia transfer to the permeate through the hydrophobic pores of the MD membrane. For this reason, the MD application is limited to membrane-based ammonia stripping (condensing \(\text{NH}_4^+\) on the permeate side) to recover ammonia from highly concentrated ammonia wastewater such as source-separated human urine or swine manure (Tun et al. 2016). Table 3 summarizes the advantages and disadvantages of membrane distillation.

### 4. Membrane gas separation

Table 4 summarizes the advantages and disadvantages of membrane gas separation (Baker et al. 2010; Baker 2012; Chowdhury 2011).

Mainly polymeric materials are used in industrial gas separation processes (Chowdhury 2011). Materials science research has expanded the range of membrane materials that can be applied. Rybak and Kaszuwara (2015) produced magnetic hybrid membrane for air separation based on ethylcellulose (EC), poly(2,6-dimethyl-1,4-phenylene

### Table 2  Pros and cons of stripping and absorption (Başakçilardan-Kabakci et al. 2007; Minocha and Rao 1988; Perry et al. 1997)

| Stripping and absorption |   |
|--------------------------|--|
| **Pros**                 | **Cons**                               |
| Generates two fertilizer products, magnesium ammonium phosphate (MAP or struvite, solid form) and ammonium sulphate (liquid form) | Need of sulphuric acid for the reaction |
| Solubility of ammonia is an advantage only if the pH is sufficiently low in the case of absorption | High air flow rates should be used in air stripping |
| 97% of ammonia can be stripped in a counter currently operated packed column having a diameter of 1 m and a packing height of 2.5 m | Theoretically high absorption rate is expected since ammonia absorption into an acid solution is limited by the gas phase mass transfer |
oxide) (PPO), various magnetic praseodymium and neodymium powder microparticles as fillers (Rybak et al. (2016)). Various magnetic inorganic–organic hybrid membranes based on linear or hyperbranched polyimide matrix and magnetic microparticles were prepared by Rybak et al. (2017). Polyimide mixed-matrix membranes with high thermal and mechanical stability can be also capable for gas separation (Rybak et al. (2014). 

Due to much higher packing densities and widespread industrial uses for membrane-based gas separations, hollow-fibre membrane modules are the focus of the modelling efforts (Chowdhury 2011). The steady-state modelling of a gas membrane separator can be utilized:

- to investigate and study the effect of various operating conditions on the process behaviour
- to design commercial scale modules and to scale up from pilot plant to large-scale units
- to conduct process optimization and
- to investigate alternative processes using process simulator (Ahsan 2016).

The ammonia recovery of hydrophobic gas-permeable membrane is based on the following core idea. Ammonium–ammonia balance shifts towards ammonia in alkaline pH range, which is a soluble gaseous compound. Ammonia can pass through the membrane because there is always an NH$_3$ concentration gradient over the membrane, as it can be seen in Fig. 1 (Kaljunen 2018).

The gradient remains constant because of the NH$_3$ inside the membrane reacts by adding sulphuric acid (H$_2$SO$_4$) to form ammonium sulphate [(NH$_4$)$_2$SO$_4$], rendering NH$_3$ concentration inside the membrane to zero (Kaljunen 2018). The NH$_3$ can be reacted with H$_2$SO$_4$ in Eq. (2):

![Fig. 1 Gas-permeable membrane function principle for ammonia recovery [modified sketch by (Kaljunen 2018)]](image_url)

Table 3 Pros and cons of membrane distillation (Fane et al. 1987; Pangarkar et al. 2016; Tun et al. 2016)

| Membrane distillation | Cons |
|-----------------------|------|
| The product can be pure | The MD application is limited to membrane-based ammonia stripping (condensing NH$_4^+$ on the permeate side) to recover ammonia |
| It can operate with modest temperature driving force. | It has high initial cost |
| It is not significantly limited by osmotic pressure effects | Sediments and particles go through the membrane will clog up the membrane surface |

Table 4 Pros and cons of membrane gas separation (Chowdhury 2011; Drioli and Romano 2001; Lokhandwala et al. 2010; Mulder 1996)

| Membrane gas separation | Cons |
|-------------------------|------|
| Low environmental impacts due to the absence of chemical additives, etc., and usually high quality of final products | Fouling due to contaminated feed |
| Hybrid process: in the same facility, it can be combined easily with other separation methods | Expensive fabrication method |
| On laboratory or pilot-scale data, easy to scale up due to modular design of membrane | Incapability to handle corrosive substances |
| Lower energy requirement, because of absence of phase and temperature change phenomena | Polymer membrane process cannot sustain high-temperature condition |
| Easy plant operation due to steady continuous process | Low maintenance costs |
| Low maintenance costs | |
$2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_3)_2\text{SO}_4$  \hspace{1cm} (2)

Figure 2 illustrates the $\text{NH}_3$ concentrations in effluent flow and acid flow, over the length of a single membrane separation run.

In start-up phase, the $\text{NH}_3$ concentration in the reactor decreases aggressively, while $\text{NH}_3$ concentration in acid is increasing in a logarithmic manner. After reaching the steady state at $t_1$, the $\text{NH}_3$ concentration in the reactor is constant until $t_2$. $T_1$ marks the end of the starting phase, and $t_2$ end of the steady state (Kaljunen 2018).

It can be summarized that struvite precipitation, air stripping and absorption, and membrane technologies have advantageous and disadvantageous properties, all of these must be considered when choosing the suitable method.

**Materials and methods**

1. **Samples**

   The properties of the wastewater (Sample I) used for the experiment are seen in Table 5. Values are calculated over the year 2016 from 52 samples. The wastewater was gained from Viikinmäki wastewater treatment plant from Helsinki, Finland.

   In Table 6, the general composition of human urine (Sample II) can be seen, where above 10 mg/L component is indicated (Putnam 1971).

2. **Laboratory apparatus**

   Figure 3 shows the laboratory test apparatus.

   The schematic representation is seen in Fig. 4.

   The parts of the equipment are the following: airtight container with cc. 5 litres sample (1), pump (2), water heating bath (3), reactor (4) and acid container (5). The reactor is a cylinder of 1.9 litres with two gas-permeable membrane tubes (Zeus Aeos™ ePTFE Extruded Special) running through the reactor. Aeos® ePTFE products from Zeus feature microscopic pores in the material structure are made by expanding PTFE under controlled conditions. The thickness of the membrane tubes is 0.495 mm. The two membranes are running in parallel. The total effective membrane surface area is 0.028 m², and the membrane surface area per reactor volume ratio is 1.47 m²/L. Reactor is decided to be in vertical position. Table 7 summarizes the main parameters of the apparatus.

3. **Experimental method**

   The experiments were implemented with a continuous reactor by the following steps: at first, the sample mixing was switched on with magnetic mixer. After that pump and 35 °C water heating bath were started. Then, the sample flowed into the water bath and entered at the top of the reactor. The sample output was at the bottom of the reactor. At last, the 1 mol/L $\text{H}_2\text{SO}_4$ (Molar Chemicals, 95–97%) flow has started and the reactor mixing with a slow-paced
magnetic mixer also. The flow inside the membrane tubes (acid flow) was directed against the liquid flow outside the membranes. Acid flow was returned to the acid container, which means the acid is circulating. The theoretical background of reaction and run is seen in Figs. 1, 2.

The following parameters were investigated and optimized regarding ammonia transfer over the membrane in the case of Sample I: acid flux, hydraulic retention time (HRT), membrane thickness with thinner membrane, acid type with 1 mol/L phosphoric or sulphuric acid and wastewater pH with 10, 11 and 12. Ca(OH)_2 powder from Nordkalk was added to sample to increase pH level. Table 8 lists all the conducted tests:

Optimal acid flow was tested by four trials with the reactor. Based on these preliminary tests, the optimal acid flux was determined to be 320 L/m² h (Mikola et al. 2017). Increasing the acid flux further would offer little benefit for the transfer rate efficiency. Furthermore, based on a trial using phosphoric acid, the acid type did not show a significant difference (Mikola et al. 2017). Thus, the experiments were conducted using sulphuric acid.

Only test run was investigated in the case of Sample II. HRT was changed, and the 120 L/m²/h H_2SO_4 flow was used.

Samples were taken out from the effluent, from the container and from the acid in every 2 h. The sample points are seen in Fig. 4. The samples from the effluent, from the container and from the acid were analysed manually with Orion 900/200 NH₃ gas sensing electrode from Thermo Electron Corporation. The applied method was standard ISO 11732. Ammonia content of both samples was measured. Further, parameters were investigated in the case of Sample I. Table 9 lists the used standard methods.

### 4. Modelling method

After laboratory measurements, based on experimental data and results of Sample I, the separation process was rigorously modelled in professional flowsheet environment and
optimized with dynamic programming optimization method (Edgar et al. 2001; Toth et al. 2015). Membrane module of ChemCAD 7.1.4 program was used with the following specifications (see Table 10):

The Membrane UnitOp is used to model polymeric membrane modules used in applications such as hydrogen recovery, nitrogen production and natural gas processing. CHEMCAD can model hollow-fibre or spiral-wound membranes. This UnitOp is used only for gas separation. Steady-state modelling in counter flow was investigated. Two hundred iterations were allowed to calculate the heat and material balances for this UnitOp. The detailed mathematical theory of membrane transport model and parameter determination can be found in paper of Coker et al. (1998). We followed the methodology of Coker et al. (1998) in counter-current case. Maxwell and Bruggeman models are also current and suitable for describing the gas permeation process through mixed-matrix membranes (Rybak et al. 2018). Figure 5 shows the model flowsheet, based on experimental apparatus (see Fig. 4).

Heat exchanger served the water heating bath. The ‘Loop’ module regulated the order of feed flows; at first,

| Table 7 Parameters of laboratory apparatus |
|-------------------------------------------|
| System parameter                          | Value   |
| Volume (L)                                 | 1.9     |
| Membrane surface area (m²)                 | 0.028   |
| Membrane surface area per volume (m²/L)    | 1.47    |
| Reactor length (m)                         | 0.45    |
| Reactor diameter (m)                       | 0.074   |
| Membrane tube diameter (m)                 | 0.01    |
| Membrane wall thickness (mm)               | 0.495   |

| Table 8 Optimized parameters of Sample I   |
|--------------------------------------------|
| Number of experiments | HRT (h) | Acid flux (L/m²h) | Acid type | Optimization          |
|------------------------|---------|-------------------|-----------|-----------------------|
| 4                      | 8       | 30–320            | H₂SO₄     | Acid flux             |
| 6                      | 2–12    | 320               | H₂SO₄     | HRT                   |
| 2                      | 8       | 320               | H₂SO₄     | pH                    |
| 1                      | 8       | 320               | H₃PO₄     | Acid type             |
| 1                      | 8       | 320               | H₂SO₄     | Membrane surface area |

| Table 9 List of standard analysing methods |
|--------------------------------------------|
| Compound | Standard, method |
|----------|------------------|
| NH₄⁺     | ISO 11732        |
| SS       | SFS-EN 872, v. 2005 |
| PO₄³⁻   | SFS-EN ISO 15681-1 |
| COD      | SFS 5594         |
| Total nitrogen | SFS-EN-ISO 11905-1 v. 1998 |
| Total phosphorus | SFS-EN ISO 6878 v. 2004 |
| TSS      | SFS 3008         |

| Table 10 Specifications of membrane module in flowsheet program |
|---------------------------------------------------------------|
| Membrane type       | Hollow fibre |
| Flow pattern        | Counter      |
| Number of parallel shells | 2           |
| Stream enters       | Shell        |
| Number of fibres    | 100          |
| Fibre length        | 0.45 m       |
| Fibre ID            | 150 μm       |
| Fibre OD            | 495 μm       |
| Pot length          | 0.1 m        |

Fig. 4 Schematic representation of experiment apparatus
‘Wastewater part’ and the ‘Acid part’ were pumped into membrane module. Non-conventional solid was used as TSS in computer program. The cc. 1 ppm phosphate was passed, and the total phosphate and non-NH4–N content were operated as organic material, because row wastewater had to be treated.

After model verification, membrane separation was optimized in computer program based on industrial data. 1.25 m high, 0.4 m length and 200-L volume reactor was investigated. 2500 m³/day wastewater had to be treated with membrane reactor.

Four parameters were optimized in flowsheet program:

1. Area/volume: effective membrane surface area/Reactor volume: 15, 20, 30, 40, 50 and 60 1/m²
2. Wastewater temperature: 20, 25, 30, 35, 40 and 45 °C
3. Acid flux: 200, 250, 300, 350, 400 and 450 L/m²h
4. HRT: 2, 4, 6, 8, 10 and 12 h.

Results and discussion

The results are divided into NH3 recovery results and secondary findings. The evaluation of optimized parameters (see Table 8) is demonstrated in the function of ammonia harvesting efficiency.

1. Experimental results

Six run were investigated with different retention times. Figure 6 shows the retention time’s effect in the function of ammonia harvesting efficiency. The NH3 harvesting efficiency is calculated by comparing ammonia concentration in effluent and initial wastewater streams.

Retention time affects the harvesting efficiency, with the tests which were carried out with wastewater showed, that harvesting efficiency not increased significantly after 8 h’ hydraulic retention time.

Three tests were investigated with different pH with the following ammonia harvesting efficiency: 40% in pH 10, 42% in pH 11 and 46% in pH 12. It can be stated that wastewater pH is relevant, because it affects the NH3–NH4+ balance (Kaljunen 2018).

One test was run by shutting down one of the two membranes inside the reactor. Figure 7 illustrates the ammonia mass transfer over the membrane on these two different situations.

The overall ammonia transfer rate is clearly higher when using two membranes, represented by dashed lines (ammonia concentration in acid) in Fig. 7. The difference in ammonia concentrations is relatively small compared to the difference of surface area: using two membranes, the ammonia concentration in acid is only 40% higher, while the membrane surface area is 100% higher. This effect is visible through solid lines (transfer rate): the transfer rate per unit surface area is more efficient when using a single membrane. This effect can be partially explained with acid flux. By shutting down one of the membranes while keeping the acid circulation rate constant, the acid flux in a single membrane tube increased. This possibly promoted ammonia transfer. However, the experiment was subject to unreliable
mixing equipment and is also possible that mixing was more efficient for the single membrane test.

It can be concluded that the pH, hydraulic retention time and acid circulation rate influencing the nitrogen recovery efficiency are relevant, while acid type does not have any significant impact on harvesting efficiency. The optimized parameters are the following: 320 L/m²h acid, 8 h HRT, pH 12 and H₂SO₄ acid. Table 11 shows the Sample I results of the optimized run.

It can be seen that all measured parameters decreased in effluent, and the highest reduction was reached in ammonia concentration. The average standard deviation of component balances in Sample I experiments was 2 mg/L. Figure 8 shows the HRT in the function of NH₃ concentration of human urine experiment.

The standard deviation of NH₃ component balance was 5 mg/L in urine measurement. It can be determined that the ammonia concentration can be decreased in effluent in both cases, and therefore, the Zeus Aeos™ ePTFE is capable for NH₃ recovery from wastewater and human urine. It can be determined that after all experiments, the applied membrane surface was not deformed, and the membranes retained their mechanical stability.

### Table 11 Results of optimized experiment of wastewater (Sample I)

| Parameter   | Wastewater | Influent | Effluent | Reduction (%) |
|-------------|------------|----------|----------|---------------|
| NH₄-N (mg/L)| 840        | 550      | 310      | 63            |
| Non-NH₄ (mg/L)| 210      | 250      | 170      | 19            |
| Total-N (mg/L)| 1050    | 800      | 480      | 54            |
| Total-P (mg/L)| 13.1     | 7.6      | 7.3      | 44            |
| SS (mg/L)   | 1290       | 1090     | 890      | 31            |

### Table 12 Comparison results of experiment and model (Sample I)

| Parameter   | Effluent |
|-------------|----------|
| NH₄-N (mg/L)| 310      |
| Organic-N (mg/L)| 170      |
| Organic-P (mg/L)| 7.3      |
| Non-conv. solid (mg/L)| 890      |

### Fig. 7 Ammonia concentration (mg/L) in acid and ammonia transfer flux (mg/m²h) over the membrane in two different surface area situations (Sample I)

### Fig. 8 Ammonia concentration in the effluent flow of human urine (Sample II)

### 2. Modelling results

The optimized experiment (see Table 11) was verified in flowsheet environment. The H₂SO₄ flow was 0.01 L/h, the wastewater stream was 0.16 L/h, and effluent water flow was 0.17 L/h, respectively. Table 12 shows the comparison of laboratory measurement and computer simulation.
The optimized experimental conditions were adjusted in flowsheet simulator, the same membrane area, temperature, etc.

It can be determined that the experiment results are in good accordance with modelling results. Table 13 shows the results of modelling optimization. Eighty-five percentage ammonia harvesting efficiency can be reached with 60 membrane surface area/reactor volume ratio, at 35 °C feed temperature, with 350 L/m²h acid and in 8 h hydraulic retention time. It can be seen that the effect of initial wastewater temperature was not significant in NH₃ harvesting efficiency.

Figure 9 combines the investigated parameters in the function of ammonia harvesting. There are six cases shown in Fig. 9: Area/Volume versus Temperature (I), Area/Volume versus Acid (II), Area/Volume versus HRT (III), Temperature versus Acid (IV), Temperature versus HRT (V) and Acid versus HRT (VI). The equations above the figures describe the mathematical relationships between the parameters.

It can be concluded that the effect of temperature is not significant, acid and HRT have the most decisive effects for ammonia harvesting efficiency.

Daguerre-Martinia et al. (2018) have investigated the nitrogen recovery from synthetic wastewater using ePTFE (Phillips Scientific Inc., Rock Hill, SC) gas-permeable membranes. Higher molar ratios inhibited the N recovery process resulting in low efficiencies (< 65%), but NH₄-N removal value was over 90% in a four-day experiment. Dube et al. (2016) used ePTFE gas separation membranes to recover ammonia from anaerobically digested swine wastewater, and the efficiency was over 90% in a five-day experiment, too. It must be mentioned that accurate comparison can be achieved with more similar raw wastewater sample. However, ammonia recovery has not been studied widely in the case of wastewater sample from communal WWTP.

### Conclusions

Hydrophobic gas separation membrane was investigated for nitrogen recovery from wastewater and human urine. Laboratory experiments were achieved with Zeus Aeos™ ePTFE membrane to verify membrane model in professional flowsheet environment. It can be stated that using gas separation, the ammonia content can be decreased from wastewater and from human urine. The model of gas separation was capable to describe the transport, and the results fitted to the experimental data. The model of wastewater separation
was optimized by dynamic optimization method. The rigorous flowsheet modelling suggests that the gas separation can reduce nitrogen concentration of wastewater, 85% ammonia harvesting efficiency can be reached. It can be also determined that our verified, adequate and optimized model can be a competitive alternative for the nutrient recovery from wastewater.

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References

Ahsan M (2016) Mathematical modeling of membrane gas separation using finite difference method. Pac Sci Rev A Nat Sci Eng 18(2):47–52

Alkhudhiri A, Darwish N, Hilal N (2012) Membrane distillation: a comprehensive review. Desalination 287:2–18

Antonini S, Paris S, Eichert T, Clemens J (2011) Nitrogen and phosphorus recovery from human urine by struvite precipitation and air stripping in Vietnam. CLEAN Soil Air Water 39:1099–1104

Baker RW (2012) Membrane technology and applications, 3rd edn. Wiley, Newark

Baker RW, Wijmans JG, Huang Y (2010) Permeability, permeance and selectivity: a preferred way of reporting pervaporation performance data. J Membr Sci 348:346–352

Başakçilardan-Kabakci S, İpekoğlu AN, Talinli I (2007) Recovery of ammonia from swine manure anaerobic digester effluent using gas-permeable membrane technology. Waste Manag 49:372–377

Edgar TF, Himmelblau DM, Lasdon LS (2001) Optimization of chemical processes, 2nd edn. McGraw-Hill, New York

Etté B (2009) Optimization of low-cost struvite recovery. M.Sc. Thesis, EPFL, Lausanne, Switzerland

Etté B, Tilley E, Khadka R, Udert KM (2011) Low-cost struvite production using source-separated urine in Nepal. Water Res 45:852–862

Fane AG, Schofield RW, Fell CID (1987) The efficient use of energy in membrane distillation. Desalination 64:231–243

Ganrot Z, Dave G, Nilsson E, Li B (2007) Plant availability of nutrients recovered as solids from human urine tested in climate chamber on Triticum aestivum L. Biorecs Technol 98(16):3122–3129

Hajós L (ed) (2005) A mezőgazdasági termelés gyakorlatának alapismeretei. Szaktudás Kiadó Ház Rt, Budapest

Huang H, Zhang P, Zhang Z, Liu J, Xiao J, Gao F (2016) Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology. J Clean Prod 127:302–310

Kaljunen J (2018) Nitrogen harvesting from liquid waste streams using hydrophobic gas permeable membranes. M.Sc. Thesis, Aalto University, Helsinki, Finland

Le Corre KS, Valsamis-Jones E, Hobbs P, Parsons SA (2005) Impact of calcium on struvite crystal size, shape and purity. J Cryst Growth 3:514–522

Lind B-B, Ban Z, Bydén S (2000) Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Biorecs Technol 73:169–174

Liu B, Giannis A, Zhang J, Chang VW-C, Wang J-Y (2015) Air stripping process for ammonia recovery from source-separated urine: modeling and optimization. J Chem Technol Biotechnol 90(12):2208–2217

Loch J, Nosticzius Á (2004) Agrokémia és növényvédelmi kémia. Mezőgazda Lap-és Könykiadó Kft, Budapest

Lokhandwala KA, Pinnau I, He Z, Amo KD, DaCosta AR, Wijmans JG, Baker RW (2010) Membrane separation of nitrogen from natural gas: a case study from membrane synthesis to commercial deployment. J Membr Sci 346:270–279

Mikola A, Kaljunen J, Pradhan SK, Aurola A-M, Vahala R (2017) Nitrogen recovery from digester reject water using selective gas-permeable membrane. In: IWA specialist conference on sustainable wastewater treatment and resource recovery. IWA, Chongqing, China

Minocha VK, Rao AVSP (1988) Ammonia removal and recovery from urea fertilizer plant waste. Environ Technol Lett 9(7):655–664

Mulder J (1996) Basic principles of membrane technology. Springer, Dordrecht

Pangarkar BL, Deshmukh SK, Sapkal VS, Sapkal RS (2016) Review of membrane distillation process for water purification. Desalin Water Treat 57(7):2959–2981

Perry RH, Green DW, Maloney OJ (1997) Perry’s chemical engineers’ handbook. McGraw-Hill, New York

Putnam D (1971) Composition and concentrative properties of human urine. NASA Contractor Report, Langley Research Center, Washington

Ronteltap M, Maurer M, Hausherr R, Gujer W (2010) Struvite precipitation from urine—influencing factors on particle size. Water Res 44:2038–2046

Rose C, Parker A, Jefferson B, Cartmell E (2015) The characterization of feces and urine: a review of the literature to inform advanced treatment technology. Crit Rev Environ Sci Technol 45:1827–1879
Rybak A, Kaszuwara W (2015) Magnetic properties of the magnetic hybrid membranes based on various polymer matrices and inorganic fillers. J Alloys Compd 648:205–214
Rybak A, Dudek G, Krasowska M, Strzelewicz A, Grzywna ZJ, Sysel P (2014) Magnetic mixed matrix membranes in the air separation. Chem Pup 68(10):1332–1340
Rybak A, Rybak A, Kaszuwara W, Awietjan S, Jaroszewicz J (2016) The rheological and mechanical properties of magnetic hybrid membranes for gas mixtures separation. Mater Lett 183:170–174
Rybak A, Rybak A, Kaszuwara W, Awietjan S, Molak R, Sysel P, Grzywna ZJ (2017) The magnetic inorganic-organic hybrid membranes based on polyimide matrices for gas separation. Compos B Eng 110:161–170
Rybak A, Rybak A, Sysel P (2018) Modeling of gas permeation through mixed-matrix membranes using novel computer application MOT. Appl Sci 8(7):1166
Tilley E, Etter B, Khadka R, Manandhar A, Shrestha RR, Udert KM (2009) Development of struvite reactors for phosphate recovery from urine in the Kathmandu Valley. IWA Development Congress, Mexico
Toth AJ, Andre A, Haaz E, Mizsey P (2015) New horizon for the membrane separation: combination of organophilic and hydrophilic pervaporations. Sep Purif Technol 156:432–443
Tun LL, Jeong D, Jeong S, Cho K, Lee S, Bae H (2016) Dewatering of source-separated human urine for nitrogen recovery by membrane distillation. J Membr Sci 512:13–20
Zhang T, Ding L, Ren H (2009) Pretreatment of ammonium removal from landfill leachate by chemical precipitation. J Hazard Mater 166:911–915

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