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ORIGINAL PAPER

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

Judit Nagy[1,2] · Juho Kaljunen[3] · Andras Jozsef Toth[4,5]

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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/m^{2}h 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

✉ Andras Jozsef Toth
ajtoth@envproceng.eu

[1] Department of Building Services and Process Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3, Budapest 1111, Hungary

[2] Department of Applied Mechanics, Faculty of Mechanical, Informatics and Electrical Engineering, Széchenyi István University, Egyetem tér 1, Győr 9026, Hungary

[3] Department of Built Engineering, School of Engineering, Aalto University, Tietotie 1 E, 02150 Espoo, Finland

[4] Department of Chemical and Environmental Process Engineering, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3, Budapest 1111, Hungary

[5] Institute of Chemistry, University of Miskolc, Egyetemváros C/1 108, Miskolc 3515, Hungary

Chemical terms

$CaCO_3$	Calcium carbonate
$Ca(OH)_2$	Calcium hydroxide
H_2SO_4	Sulphuric acid
Mg^{2+}	Magnesium ion
$MgNH_4PO_4{\bullet}6H_2O$	Magnesium ammonium phosphate hexahydrate
MgO	Magnesium oxide
N_2	Nitrogen gas
NaOH	Sodium hydroxide
NH_3	Ammonia
NH_4^+	Ammonium ion
NH_4NO_3	Ammonium nitrate
$(NH_4)_2SO_4$	Ammonium sulphate
PO_4^{3-}	Phosphate ion

Abbreviations

AGMD	Air-gap membrane distillation
BOD	Biochemical oxygen demand

CAN	The mix of ammonium nitrate and $CaCO_3$ dust
COD	Chemical oxygen demand
DCMD	Direct-contact membrane distillation
ePTFE	Expanding polytetrafluoroethylene
FA	Free ammonia
HRT	Hydraulic retention time
MD	Membrane distillation
SGMD	Sweeping-gas membrane distillation
SS	Suspended solids
UAN	Ammonium nitrate solution
WWTP	Wastewater treatment plant

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_4NO_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–thraw 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):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow \quad (1)$$

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

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	

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 [$(NH_4)_2SO_4$, 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.

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 (Derese 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 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

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

Membrane distillation	
Pros	Cons
The product can be pure	The MD application is limited to membrane-based ammonia stripping (condensing $NH4^+$ 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	
Pros	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	

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).

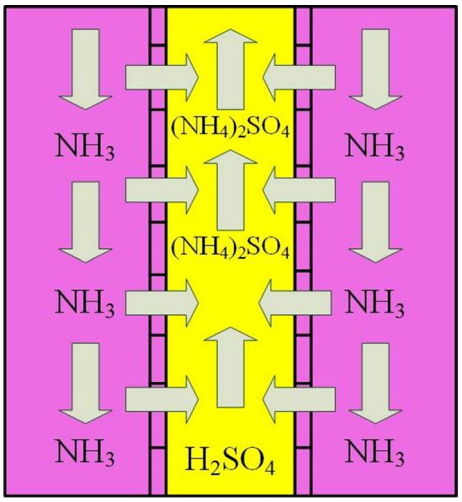

Fig. 1 Gas-permeable membrane function principle for ammonia recovery [modified sketch by (Kaljunen 2018)]

The gradient remains constant because of the NH_3 inside the membrane reacts by adding sulphuric acid (H_2SO_4) to form ammonium sulphate [$(NH_4)_2SO_4$], rendering NH_3 concentration inside the membrane to zero (Kaljunen 2018). The NH_3 can be reacted with H_2SO_4 in Eq. (2):

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \quad (2)$$

Figure 2 illustrates the NH_3 concentrations in effluent flow and acid flow, over the length of a single membrane separation run.

In start-up phase, the NH_3 concentration in the reactor decreases aggressively, while NH_3 concentration in acid is increasing in a logarithmic manner. After reaching the steady state at t1, the NH_3 concentration in the reactor is constant until t2. T1 marks the end of the starting phase, and t2 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 m^2, and the membrane surface area per reactor volume ratio is 1.47 m^2/L. Reactor is decided to be in vertical position. Table 7 summarizes the main parameters of the apparatus.

Table 5 Composition of Sample I: wastewater

Property	Average	Min	Max
BOD_7 (mg/L)	530	320	1140
SS (mg/L)	980	560	4200
Total-P (mg/L)	13	10	47
PO_4-P (mg/L)	1.4	0.5	2.7
Total-N (mg/L)	980	820	1250
NH_4-N (mg/L)	790	680	900
pH (-)	8	7.5	8.1
Alkalinity (mmol/L)	67	57	77
COD_{Cr} (mg/L)	1380	860	2100

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 H_2SO_4 (Molar Chemicals, 95–97%) flow has started and the reactor mixing with a slow-paced

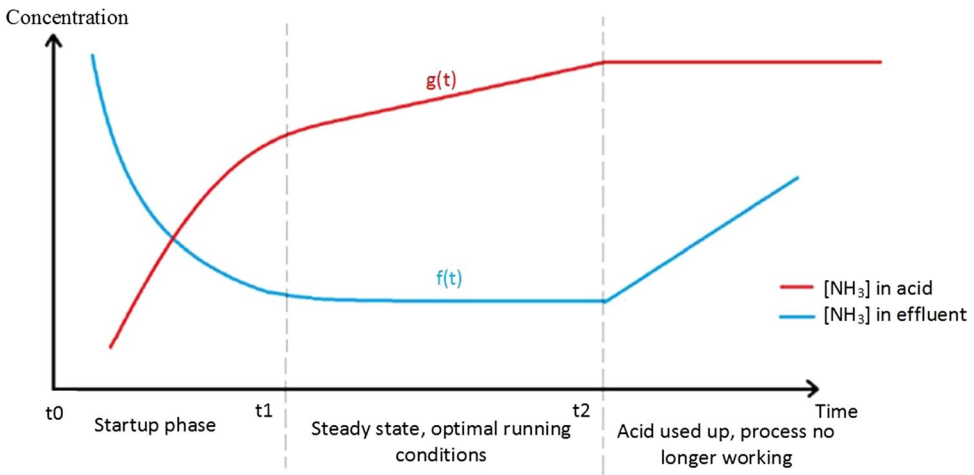

Fig. 2 Theoretical ammonia concentrations in effluent and acid [modified sketch by (Kaljunen 2018)]

Table 6 Composition of Sample II: human urine–total solutes (Putnam 1971)

		mg/L			mg/L
1	Urea	16,300	21	Histidine	185
2	Chloride	5135	22	Glutamic acid	164
3	Sodium	2780	23	1-Methylhistidine	145
4	Potassium	1680	24	Imidazole derivatives	145
5	Creatinine	1410	25	Androsterone	141
6	Sulphur, inorganic	982	26	Carbonate	125
7	Hippuric acid	860	27	Glucose	115
8	Phosphorus, total	770	28	Magnesium	113
9	Citric acid	510	29	Taurine	103
10	Glucuronic acid	475	30	Aspartic acid	89
11	Uric acid	355	31	Cystine	69
12	Uropepsin (as tyrosine)	315	32	Citrulline	65
13	Ammonia	311	33	Threonine	65
14	Bicarbonate	290	34	Lysine	58
15	Phenols	275	35	Indoxylsulphuric acid	57
16	Sulphur, organic	274	36	*m*-Hydroxyhippuric acid	51
17	Glycine	270	37	*p*-Hydroxyphenyl-hydrocrylic acid	51
18	Creatine	265			
19	Lactic acid	215			
20	Calcium	210			

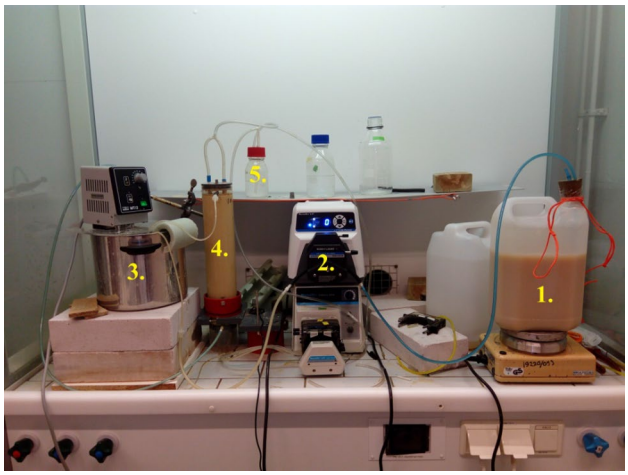

Fig. 3 The experimental apparatus with gas-permeable hydrophobic membrane

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/m^2 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/m^2/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 NH_3 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

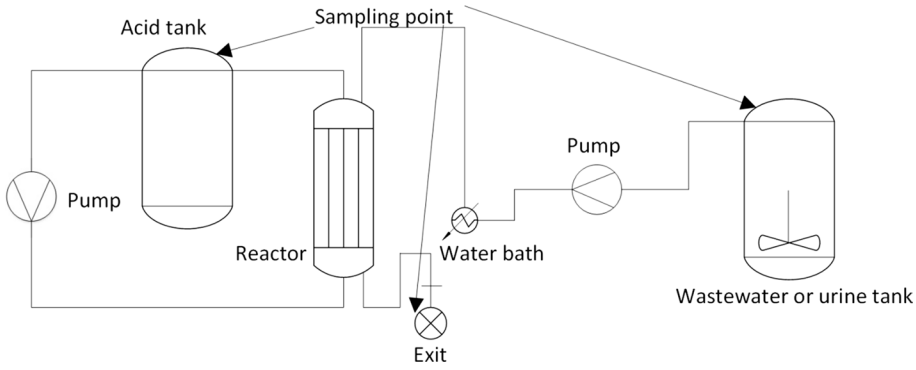

Fig. 4 Schematic representation of experiment apparatus

Table 7 Parameters of laboratory apparatus

System parameter	Value
Volume (L)	1.9
Membrane surface area (m^2)	0.028
Membrane surface area per volume (m^2/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 9 List of standard analysing methods

Compound	Standard, method
NH_4^+	ISO 11732
SS	SFS-EN 872, v. 2005
PO_4^{3-}	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

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).

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

Heat exchanger served the water heating bath. The 'Loop' module regulated the order of feed flows: at first,

Table 8 Optimized parameters of Sample I

Number of experiments	HRT (h)	Acid flux (L/m^2h)	Acid type	Optimization
4	8	30–320	H_2SO_4	Acid flux
6	2–12	320	H_2SO_4	HRT
2	8	320	H_2SO_4	pH
1	8	320	H_3PO_4	Acid type
1	8	320	H_2SO_4	Membrane surface area

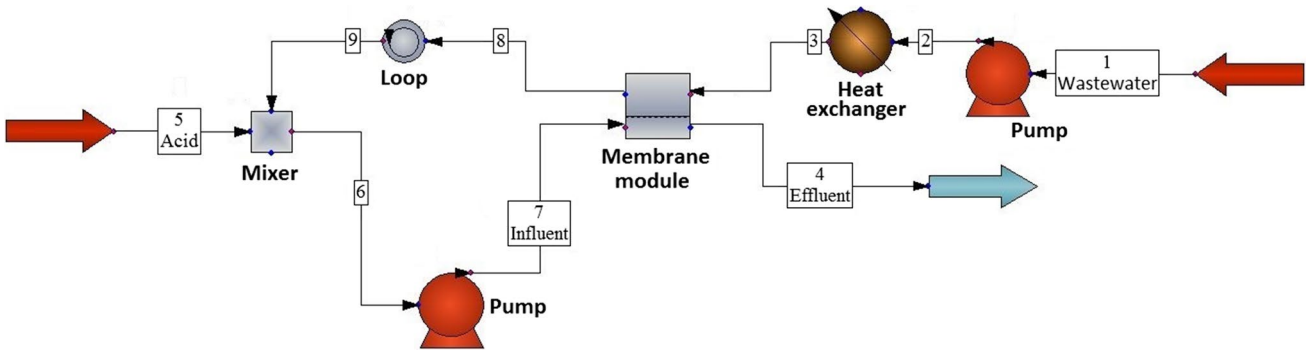

Fig. 5 Flowsheet of membrane model

'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-NH_4–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 m^3/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/m
2. Wastewater temperature: 20, 25, 30, 35, 40 and 45 °C
3. Acid flux: 200, 250, 300, 350, 400 and 450 L/m^2h
4. HRT: 2, 4, 6, 8, 10 and 12 h.

Results and discussion

The results are divided into NH_3 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 NH_3 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.

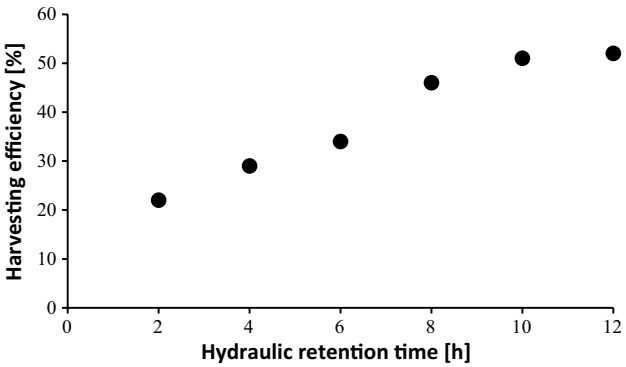

Fig. 6 Ammonia harvesting efficiency in the function of hydraulic retention time (Sample I)

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 NH_3– NH_4^+ 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

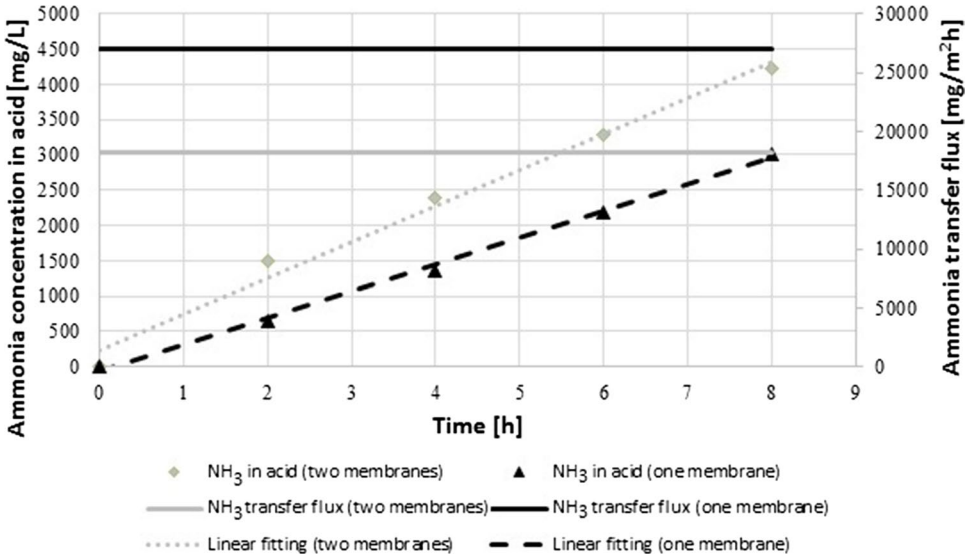

Fig. 7 Ammonia concentration (mg/L) in acid and ammonia transfer flux (mg/m^{2}h) over the membrane in two different surface area situations (Sample I)

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

	Wastewater	Influent	Effluent	Reduction (%)
NH_4-N (mg/L)	840	550	310	63
Non-NH_4 (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

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/m^{2}h acid, 8 h HRT, pH 12 and H_2SO_4 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 NH_3 concentration of human urine experiment.

The standard deviation of NH_3 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 NH_3 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.

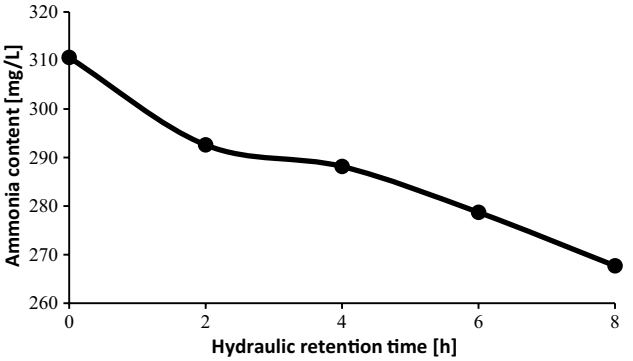

Fig. 8 Ammonia concentration in the effluent flow of human urine (Sample II)

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

	Effluent	
	Experiment	Model
NH_4-N (mg/L)	310	290
Organic-N (mg/L)	170	165
Organic-P (mg/L)	7.3	8
Non-conv. solid (mg/L)	890	900

2. Modelling results

The optimized experiment (see Table 11) was verified in flowsheet environment. The H_2SO_4 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.

Table 13 Optimization results of gas separation membrane modelling (Sample I)

	Area/volume (1/m)	Temperature (°C)	Acid (L/m^{2}h)	HRT (h)	NH_3 harvesting efficiency (%)
1	15	35	350	8	63
2	20	35	350	8	68
3	30	35	350	8	71
4	40	35	350	8	74
5	50	35	350	8	78
6	60	35	350	8	85
7	60	20	350	8	82
8	60	25	350	8	83
9	60	30	350	8	83
10	60	35	350	8	85
11	60	40	350	8	85
12	60	45	350	8	85
13	60	35	200	8	45
14	60	35	250	8	63
15	60	35	300	8	76
16	60	35	350	8	85
17	60	35	400	8	73
18	60	35	450	8	69
19	60	35	350	2	30
20	60	35	350	4	42
21	60	35	350	6	67
22	60	35	350	8	85
23	60	35	350	10	78
24	60	35	350	12	73

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/m^{2}h acid and in 8 h' hydraulic retention time. It can be seen that the effect of initial wastewater temperature was not significant in NH_3 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 NH_4–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

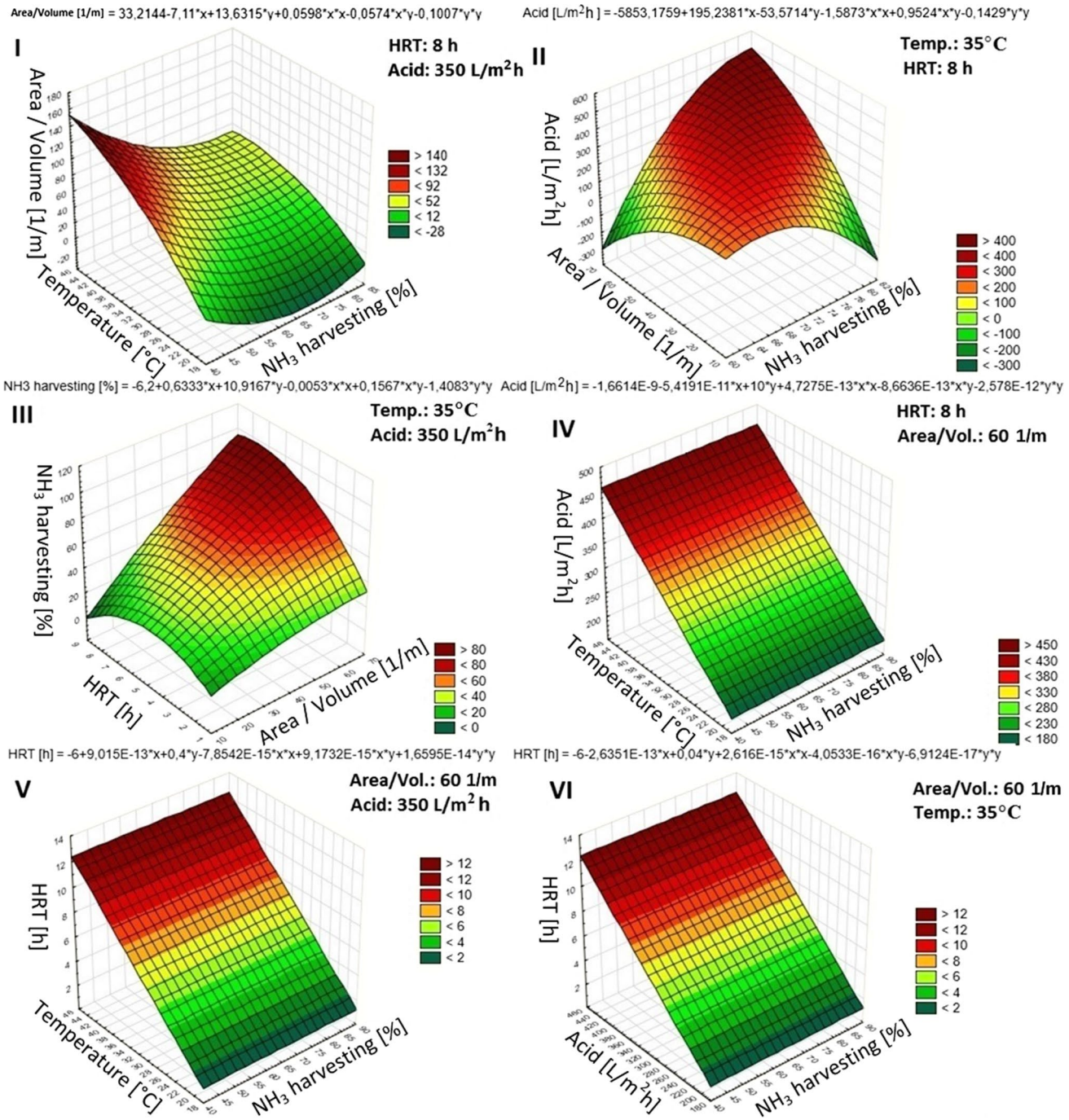

Fig. 9 Ammonia harvesting efficiency effects on changing parameters

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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