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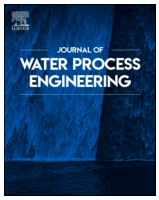

Nutrient concentration of blackwater digestate using an air gap membrane distillation process

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ABSTRACT

Blackwater from vacuum toilets contains significant amounts of nutrients that can be repurposed as fertilizer. This study aimed to evaluate an air gap membrane distillation process to concentrate nutrients in blackwater digestate. In the first experiments, various temperatures (40 °C, 55 °C and 70 °C) and pH levels (2.5, 2.8, 3.0, 4.0 and 6.0) were tested on the feed, resulting in operating conditions of 55 °C and pH 4 for the study's second experiment. Under these conditions, a 15-fold volume reduction was achieved. In this second experiment, the average permeate flux was 1.95 Lm^{-2} h^{-1} during the first 18 h, decreasing to 0.81 Lm^{-2} h^{-1} after 150 h of operation. The membrane was cleaned when the flux dropped to 0.39 Lm^{-2} h^{-1}. The final concentrate had an NPK elemental weight ratio of 1:3:0.3. A chemical model indicated that most ammonium and phosphorus were dissolved in the concentrate, with some phosphate compounds precipitating. The product contained essential micronutrients and low levels of harmful substances like As, Hg, Cd, and Pb, with NaCl at 0.3 % of the weight. The main challenge was membrane wetting, leading to 33 % of nitrogen loss and 13 % of phosphorus loss. Despite the challenges the process successfully produced a nutrient-rich concentrate beneficial for agriculture.

1. Introduction

The nutrients most used in agriculture are nitrogen (N), phosphorus (P), and potassium (K), along with secondary macronutrients such as sulphur (S), calcium (Ca), and magnesium (Mg). About 88 % of the 750,000 t/year of ammonia (used to provide nitrogen) produced worldwide is synthesised from air and hydrogen, where the energy sources used in the production are mainly natural gas or coal [1]. Phosphorus, on the other hand, is primarily produced from phosphate rock, a non-renewable resource. It has been estimated that 70 % of the high-grade rock available for agriculture will have been irreversibly depleted by 2040 [2,3]. This will lead to the exploitation of low-grade ores, resulting in increased energy use, and more mining waste [4]. Potash, a soluble form of potassium, comes also from mining sources and its availability could be constrained due to its increasing demand and only a few countries extract it [5]. Additionally, sulphur is obtained mostly from mines with the Frasch method, where sulphur is melted with superheated water (140–160 °C) underground, where the leachate pH may lead to some phytotoxic effects [6]. Calcium can be precipitated from seawater with flocculation at high pH [7], or extracted from calcite or dolomite. Plants additionally need micronutrients, such as zinc, copper, and molybdenum, which are often available in the soil. However, in several parts of the world, conventional fertilisation does not provide micronutrients, and this can result in hidden hunger due to the lack of micronutrients in food [8].

Globally, around 50 % of wastewater is discharged into water bodies without treatment [9]. Where wastewater is treated, to protect the environment and human health, some of the nutrients are still discharged to receiving water bodies, the atmosphere, or a share of the nutrients end up in the sludge, which is often disposed of or used in agriculture fields. Most of the nutrients in our diet end up in toilet wastewater (blackwater). Faeces and urine are the source of around 97 % of the nitrogen, 90 % of the phosphorus, and >65 % of the potassium in domestic wastewater [10]. The phosphorous available in blackwater could account for 22 % of global fertilizer demand [11], thus separate collection and treatment of blackwater could be a sustainable strategy

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for controlling nutrients in new urban developments. It has been shown that the collection of blackwater in pipes separate from the rest of the domestic wastewater system could potentially increase biogas production by 70 % while also potentially increasing nutrient recovery [12].

A source-separation wastewater system has been constructed in the new urban development Oceanhamnen in Helsingborg (Sweden) treated in Recolab, in which separate collection and treatment of blackwater and greywater takes place. This city district has around 350 apartments, two restaurants, three office buildings, and a hotel. The first inhabitants moved in in 2020 and the hotel opened in 2022. The blackwater is collected separately using vacuum toilets, which require 0.5–1 L per flush. Biogas is then produced from the blackwater. The water fraction remaining after this process is the blackwater digestate liquid fraction. Subsequently, struvite is precipitated, and ammonium sulphate can be produced by ammonia stripping. This system can recover 86 % to 92 % of the phosphorous and 27 % to 89 % of the more than a conventional treatment plant [12]. Nevertheless, ammonia stripping is energy-intensive and requires sodium hydroxide and sulfuric acid. Although the processes employed in Helsingborg can recover a reasonable proportion of the nitrogen and phosphorous, there are other nutrients in the digestate, such as potassium, sulphur, and micronutrients, which the process currently used in Helsingborg does not recover to any meaningful extent.

An alternative method for recovering all the nutrients in blackwater in a concentrated form is to apply membrane distillation (MD) to the blackwater digestate liquid. MD is a technology which has mainly been studied for its use in the production of potable water by desalinisation, therefore, several pilot plants and a few full-scale plants have been built [13]. It is known as a separation process, which can concentrate non-volatile solutions to their saturation point without significantly decreasing the permeate flux [14]. Furthermore, MD is not limited by osmotic pressure as is the case with reverse osmosis [15,16]. MD works using a thermal gradient process, where the heat source could be derived from solar, geothermal, or even waste heat [14,17], operating at temperatures between 30 °C and 90 °C [17]. Hot water is transported as vapour through the micropores of the hydrophobic membrane because of the vapour pressure gradient occurring on both sides of the membrane [18]. Air gap MD is a configuration in which pressurised air flows between the membrane and the condensate plate. This configuration reduces the parasitic heat loss, improves the flux, and achieves electrical and thermal consumptions of 0.13 and 90kWh/m^3, respectively, for desalinisation, where the permeate is the product of interest [17,19]. For nutrient concentration, however, the retentate is the main product of interest while the permeate could be a possibly interesting by-product. So far there are limited number of studies on nutrient concentration with membrane distillation [20,21].

One challenge with the concentration of nutrients in blackwater digestate is that most of the nitrogen present in this water is in the form of ammonium, which is a volatile compound. The ammonium-ammonia equilibrium is pH, temperature, and pressure-dependent. Only a few studies have looked at the retentate as the main product of interest in air-gap MD. One study was able to concentrate a mixture of different solid biowaste digestate to 50 % of the original volume by stabilising the ammonium through the addition of sulfuric acid to obtain a resultant solution with a pH of 2.62 and use of a hot stream at 60 °C [22].

The objectives of this study were to estimate the operating parameters, temperature and pH, for an air gap membrane distillation process, and evaluate the concentration capacity, the quality of the concentrated blackwater liquid digestate including the chemical speciation and discuss the potential use of the concentrate and permeate.

2. Materials and methods

2.1. Blackwater digestate

The liquid blackwater digestate was obtained from an up-flow anaerobic sludge blanket (UASB) digester for blackwater from Oceanhamen treated in RecoLab, Helsingborg, Sweden. The effluent of the UASB was collected in a 1 m^3 IBC tank, which was transported to the laboratory at Luleå University of Technology. The digestate was filtered with a 5 μm polymeric bag filter upon arrival at the laboratory. After filtration, the digestate was stored outdoors during spring (−5 °C to 10 °C) and summer (9 °C to 25 °C), and indoors during autumn and winter, to prevent the water from freezing. The IBC tank had an opaque cover to prevent photosynthesis during the outdoor storage period.

2.2. Quality of the blackwater digestate to be concentrated

The blackwater digestate was received in two 1 m^3 batches for all three phases and another batch (1 m^3) for phase 3. The batches were filtered through a 5 μm filter and analysed over a range of parameters (Table 1). Most of the nitrogen was in the form of ammonium, while the levels of nitrite and nitrate were below the reporting limits. Volatile fatty acids were not found in the two batches for phase 1 and phase 2, but 79.8 mg/L of acetic acid and 0.61 μg/L vinyl chloride were found in the feed for the phase 3 and these compounds may cross the membrane, but they were not found on the permeate or concentrate. The difference between TOC and DOC indicated that the organic carbon was mainly particulate in the case of the concentration experiment, while phase 1 and phase 2 the organic matter had a higher portion of dissolved organic carbon. The batch for the phase 3 revealed metals important for fertilisers, such as magnesium, calcium, and potassium, to be present in the digestate. Metals restricted in fertilisers, such as cadmium and mercury, were below reporting limits.

2.3. Air gap membrane distillation set-up

In this study, an air gap membrane distillation unit with recirculation of the retentate was used (Fig. 1). The cabinet that included thermometers (manufactured by PM Plast, Sweden), flow sensors (GF Signet 3–2100-1H Turbine Flow Sensor, Switzerland), the boiler and the pumps (manufactured by Iwaki Sverige AB, Sweden) was provided by Circular Water Technologies AB. They also provided the membrane modules (Fig. 2). For the last experiment or phase 3 an additional peristaltic pump (Watson Marlow 520S) was used to refill the boiler. The tank under the boiler was originally intended for permeate collection but was not used. On the screen was possible to see the sensor outputs, which included the hot side temperatures and flows of the inlet and outlets and on the cold side the temperature at the entry and flows at the inlet and outlet. On the screen was also indicated the temperature in the boiler.

Two membrane modules were used for the experiments, although most of the experiments were performed using Module 1. Module 2 was only used when Module 1 underwent a cleaning procedure during the last experiment, the phase 3. The modules' characteristics are shown in Table 2.

Tap water was used for cooling on the cold side in the air-gap membrane distillation set-up. The temperature of the tap water varied from 7.5 °C to 13.8 °C because of seasonal variations. The hot side was heated with a warm mesh placed in the bottom of the boiler. The hot temperature was fixed at 40 °C, 55 °C and 70 °C, but during the experiments, the actual temperature measured was 2–8 °C below the fixed value. 1. The air gap pressure was fixed at 6 bar with a GEMÜ 610, Pneumatically operated diaphragm valve. The pressure was selected before the experiments by the supplier of the cabinet and was based on a pre-test where the highest permeate flux was obtained at this pressure. A possible explanation for obtaining the highest flux at 6 bar was a trade trade-off between the air gap pressure resistance and the reduction of conductive heat loss.

2.4. Study design

Three different experiments were carried out. An initial pre-

Table 1
Quality of the feed after 5 μm filtration prior to the three membrane distillation experiments.

Parameter	Unit	Phase 1		Phase 2		Phase 3	
						experiment	
Total suspended solids	mg/L	3.2		3.3		3.1	
Turbidity	NTU	110		207		339	
pH	–	7.7		7.8		7.7	
Conductivity	mS/m	996		968		982	
Alkalinity	mg HCO_3−/L	4520		4490		4630	
DOC	mg/L	180		166		22.8	
TOC	mg/L	210		280		300	
BOD 7	mg/L	207		207		336	
COD-Cr	mg/L	930		930		1150	
Total N	mg/L	1120		1000		1030	
NH_3-N + NH_4-N	mg/L	1440		1130		1060	
Total P	mg/L	78.5		160		88.4	
PO_4-P	mg/L	74.0		64.8		59.7	
Total S	mg/L	33.8		46.6		30.9	
SO_4-S	mg/L	11.3		15.6		10.3	
Metals		Total	Dissolved	Total	Dissolved	Total	Dissolved
Al	mg/L	18.6	19.7	22.1	18.3	36.1	18.0
Ca	mg/L	33.5	34.2	49.4	43.0	47.4	42.3
Cd	μg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Co	μg/L	0.32	0.16	0.34	0.0713	0.299	0.118
Cr	μg/L	<0.50	<0.50	0.818	0.595	1.29	0.679
Cu	μg/L	47.7	11.4	11.4	18.4	29.2	3.8
Fe	mg/L	0.0962	0.0374	0.142	0.0669	0.242	0.0345
Hg	μg/L	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
K	mg/L	268	282	330	293	321	291
Mg	mg/L	13.5	15	9.17	8.03	27.7	22.7
Mn	μg/L	9.41	15	15	7.26	9.41	7.04
Mo	μg/L	0.93	0.78	1.7	<0.50	1.39	<0.50
Na	mg/L	329	350	380	331	320	317
Ni	μg/L	5.0	5.8	6.3	4.2	6.5	5.0
Pb	μg/L	0.22	<0.20	0.68	0.25	0.25	<0.2
Zn	μg/L	23.3	8.36	8.36	16.1	85.4	8.05

experiment with tap water was carried out to observe the permeate flux and permeate conductivity. Then an operation parameter experiment (phase 1 and phase 2) was carried out, in which the effect of pH and temperature on the concentration process was investigated. This made it possible to determine a suitable pH and temperature to be used in phase 3, with the aim to evaluating the concentration capacity of the membrane.

2.4.1. Tap water runs and membrane cleaning procedure

The pre-experiments were carried out with the membrane modules with tap water to determine the permeate flux and the conductivity on the permeate side. The tap water on the experimental side was around 150 μS/cm. For Module 1, the permeate flux obtained from tap water was 1.97 $Lm^{-2}\ h^{-1}$, 3.69 $Lm^{-2}\ h^{-1}$ and 4.65 $Lm^{-2}\ h^{-1}$ at temperatures 40 °C, 55 °C and 70 °C, respectively. The permeate conductivity for Module 1 with tap water was in the range 5–12 μS/cm. Module 2 was tested only at 55 °C with a permeate flux of 1.85 $Lm^{-2}\ h^{-1}$and a permeate conductivity of 2.6 μS/cm. The manufacturer claimed that the membrane hydrophobicity would be acceptable if the permeate conductivity was under 50 μS/cm.

The membrane was cleaned when the permeate flux was reduced to a fifth of its original value. Cleaning was performed twice between the phases 1 and phase 2. More details of the cleaning procedure are found in the supplementary material (S1).

2.4.2. Phase 1 and phase 2

The first 2 phases aimed to find suitable operating conditions (pH and temperature) for concentrating blackwater digestate using membrane distillation, where the main quantities measured in response to changes in the operation parameters were the ammonium concentration in the permeate and the permeate flux. A randomised 2^2-factorial experiment (significant level is $\alpha = 0.05$) with three centre points was carried out, resulting in a total of 7 experiment runs (Table 3). The pH was adjusted using 85 % orthophosphoric acid and ranged from 2.5 to 6. This acid was chosen because phosphate is a macronutrient. The temperatures used during testing were 40 °C, 55 °C and 70 °C.

After carrying out the seven runs, it was apparent that working at a high pH (pH 6) led to the loss of hydrophobicity of the membrane and thus to losses of ammonium to the permeate. Consequently, four more runs (phase 2) were carried out to complement the investigated pH range, with test runs at pH 3 and pH 4 in addition to two more runs at pH 2.8 (Table 3). The phase 2 tests were carried out at 55 °C, which was a suitable temperature given the permeate flux, loss of water due to evaporation, and energy use during phase 1.

The runs were stopped once the water level in the heating tank was just above the pump inlet. The method of controlling this was imprecise, which meant that the final concentrate volume varied slightly between runs, affecting the degree of concentration achieved in each run. The permeate was sampled at the end of each experiment run.

Samples were taken from the blackwater digestate immediately after 5 μm filtration (Table 1), but also before the membrane distillation tests started, including samples before and after pH adjustment. The retentate (concentrate) and permeate samples were taken when the experiment runs ended, and the tanks were emptied.

2.4.3. Phase 3

In this experiment, a larger amount of the blackwater digestate liquid was concentrated, 100 L. The experiment setup was similar to that used for the first two phases, but the boiler had a maximum capacity of 50 L so an additional tank with 50 L was connected to the boiler. The water in this tank was pumped at a similar speed to the permeate flux. The permeate quality changes over time, therefore the permeate collection was divided into 10 batches of different volumes, which were analysed to understand the variation in permeate quality.

Concentrate samples were taken at the end of the experiment. The membrane was cleaned once during this experiment, when 20 L of the

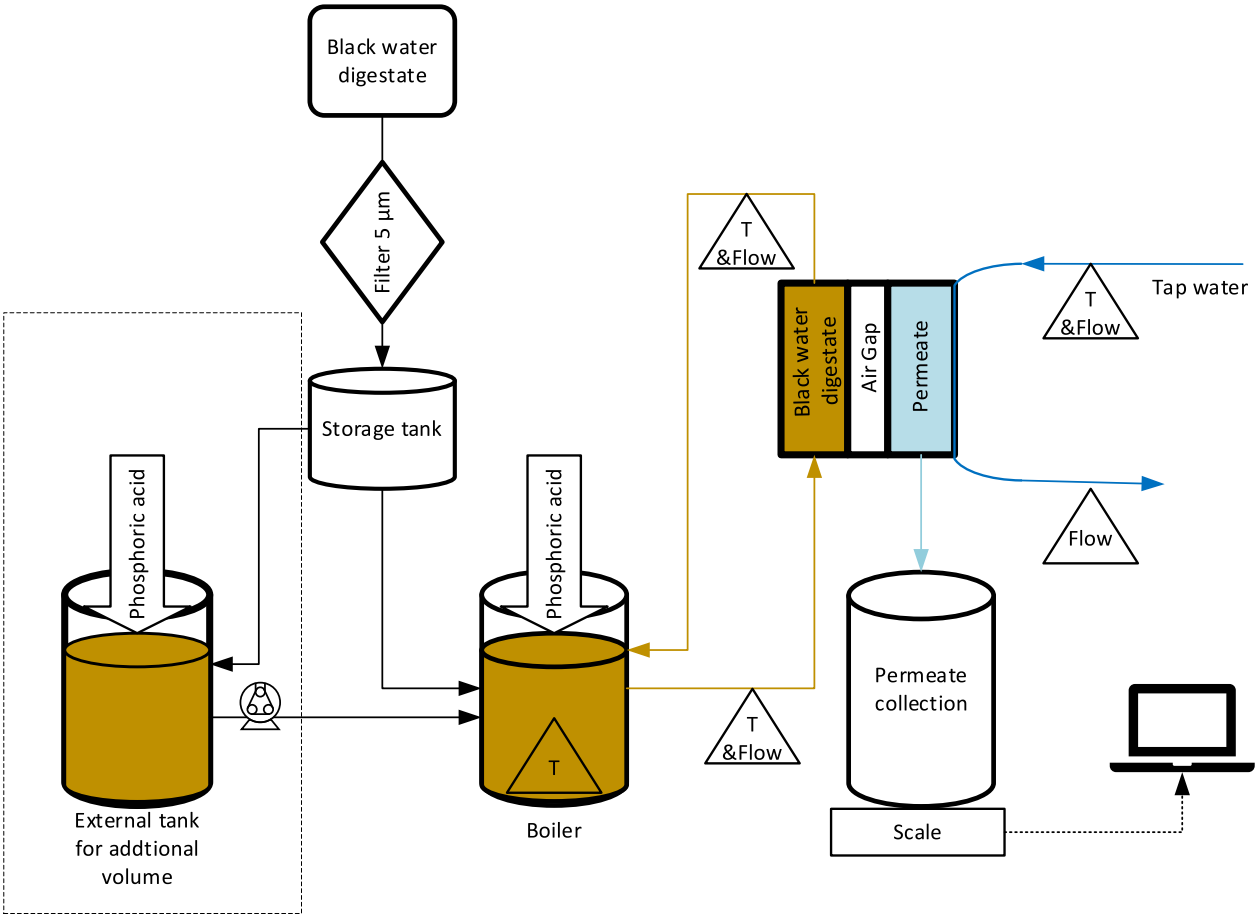

Fig. 1. Experimental set-up for the three phases. Triangles indicate sensors for temperature (T) and flow. The dashed box indicated the external tank used for phase 3.

concentrated digestate was left, due to a decrease in the permeate flux of 6 times. Due to the tank's design, it was impossible to empty the boiler completely after the end of the experiment; thus, some concentrated digestate volume was left. A known volume of tap water was used to rinse the tank.

2.5. Permeate flux measurements

The permeate flux was continuously calculated using a Defender 5000 scale, coupled with an i-DT6XWE Indicator made by OHAUS. The mass was logged every minute using the software SPDC Pro by OHAUS. The average of the permeate flux was calculated from 100 mL to 4000 mL collected in the permeate tank divided by time. During the first few minutes of operation, the flux was slower, and 4000 mL was used because the experiments at 70 °C lost much more water through evaporation and had to be stopped earlier.

2.6. Chemical analyses

In this study, total nitrogen, total Kjeldahl nitrogen, nitrite, nitrate, phosphate, total phosphorus, alkalinity, TOC, and total suspended solids were analysed as well as the elements Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, S and Zn. Details about the analysis methods can be found in supplementary material (S2).

2.7. Chemical modelling

Chemical modelling was carried out with Visual MINTEQ 4.0 [23] to estimate the effect of the addition of phosphoric acid to the blackwater digestate (feed), and to get an understanding of formation of solids and gases in the end of phase 3 of the experiment.

[23] The chemical composition measured in the digestate or concentrate solutions, the atmospheric pressure, and the possible solids formed were considered as input. Precipitation of solids was assessed with the support of the saturation index of different solid phases and the concentration of the corresponding components. The potential forming solids were selected to fit the experimental results with total and dissolved metal concentrations and with concentrations of total phosphorous and dissolved phosphate. For the feed, a titration simulation from pH 8.6 to 2.9 was conducted with the addition of phosphoric acid at 85 % to investigate the solid formation. The simulated titration was carried out to get an indication of which specific precipitates were formed, and about ammonia formation at different air pressures. The blackwater digestate is a complex matrix and the simulations of solids formation during the titration was constrained due to the limit of iterations allowed by the software. Therefore, the titration excluded the organic matter, and the number of possible solids were reduced in the model by only including the solids with highest saturation index, which were hydroxyapatite, strengite, gibbsite, struvite, and ferrihydrite.

Precipitates and gases formed in the concentrate produced in phase 3 were simulated. The solid fraction of the organic matter included in the chemical model was considered to be the difference between TOC and DOC in the concentrate. It was also assumed that the reactive organic matter was mainly constituted by humic acids and was included in the modelling calculations using the model of NICA-Donnan and the generic parameters, available in Visual Minteq 4.0 [23]. To assess possible gas formation, a simulation for each oxidation state of sulphur, S(IV), S(-II) and S (0), was done, assuming that all of the sulphur that was not

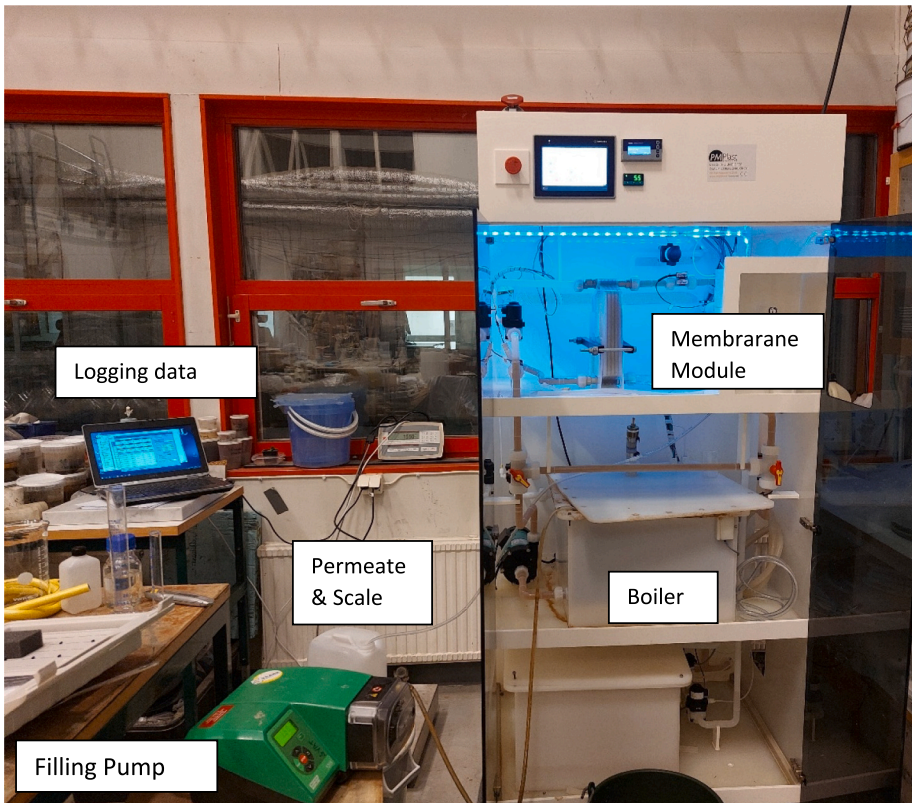

Fig. 2. Photo of the operation of phase 3.

Table 2
Characterisation of the two membrane modules used in the experiments.

Characteristics	Module 1	Module 2
Total membrane surface	0.36 m^2	0.36 m^2
Number of cassettes per module	10	10
Membrane material	Polytetrafluoroethylene (PTFE)	Polytetrafluoroethylene (PTFE)
Cassette material	Polyvinylidene fluoride (PVDF)	Polypropylene (PP)
Membrane geometry	Flat sheet	Flat sheet
Membrane thickness (mm)	0.2	0.2
Membrane pore size (μm)	0.2	0.1
Porosity (%)	80	80
Air gap (mm)	0.5–1	0.5–1
Condensation plate material	PVDF	PP

Table 3
Factorial design of phase 1 and phase 2.

	Exp name	Run order	Temperature (°C)	pH
Phase 1	N1	4	40	6
	N2	5	70	6
	N3	1	40	2.5
	N4	3	70	2.5
	N5	6	55	2.8
	N6	2	55	2.8
	N7	7	55	2.8
Phase 2	N8	8	55	2.8
	N9	9	55	2.8
	N10	10	55	3.0
	N11	11	55	4.0

forming sulphate was in only one of those oxidation states for each simulation.

It must be remarked that this chemical model showed the speciation in equilibrium conditions and closed systems, and there are more possible elements present in the blackwater digestate that were not evaluated. Also, microbiological activity and redox were not included in the model, only the oxidation state of sulphur was considered relevant for the gas formation of the concentrate in phase 3.

3. Results

3.1. Effect of operating temperature and pH on permeate flux and ammonium losses

A factorial design for the OPEs was intended for phase 1. A linear regression for the factorial experiment showed that the proton concentration significantly ($\alpha = 0.05$) increased the concentration of ammonium in the permeate while no significant temperature effect could be found. This was possible because this statistical model did not include the run order. If comparing the permeate fluxes of the runs N1 (1.70 $Lm^{-2}\ h^{-1}$) and N3 (2.33 $Lm^{-2}\ h^{-1}$) in Fig. 3, which were both ran at 40 °C, it can be seen that the average flux of N1 was lower than N3, which was the first run performed. The same trend could be seen for runs N6, N5 and N7, operated at 55 °C. Even more pronounced this trend was for phase 2, in which all runs were performed at the same temperature. This indicated that the run order had a clear effect, most probably due to scaling, which could explain why there was no statistical evidence that the flux depended on the temperature in the phase 1 experiment, even though it is known that the flux depends on temperature [24].

Fig. 4 shows the concentration of ammonium and total phosphorous in the feed, concentrate and permeate for the different runs of the operating parameter experiments (phases 1 and 2). The total phosphorous in the blackwater digestate was primarily in the form of phosphate, both before and after the addition of acid. However, the use of

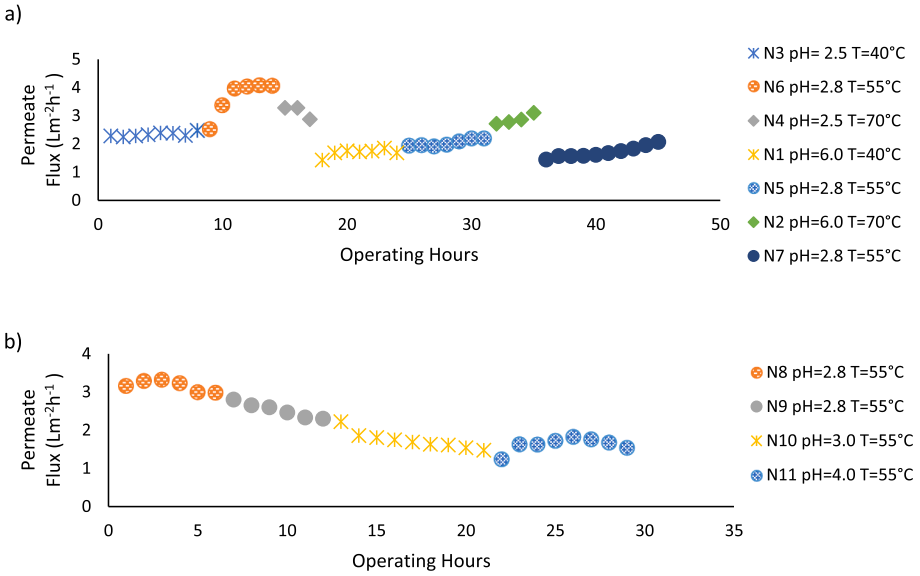

Fig. 3. Measured permeate flux during a) the experiments of phase 1 (experimental runs N1-N7) and b) experiment of phase 2 (experimental runs N8-N11) plotted against operating hours. Membrane cleaning was only carried out between phases 1 and 2.

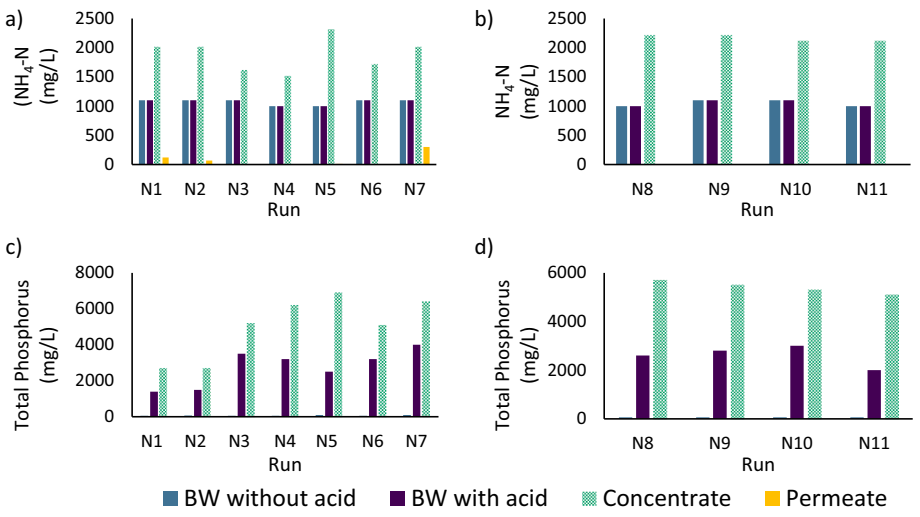

Fig. 4. The concentration of ammonium (NH_4-N) and total phosphorus in the blackwater digestate (BW) (without and with acid), in the concentrate and in the permeate. Ammonium is shown in a) phase 1, b) phase 2, c) shows total phosphorus in phase 1 and d) in phase 2. The operating conditions for the different runs were: N1: $T = 40$ °C, pH = 6; N2: $T = 70$ °C, pH = 6; N3: T = 40 °C, pH = 2.5; N4: $T = 55$ °C, pH = 2.8; N5: T = 55 °C, pH = 2.8; N6: T = 55 °C, pH = 2.8; N7: T = 55 °C, pH = 2.8; N8: T = 55 °C, pH = 2.8; N9: T = 55 °C, pH = 2.8; N10: T = 55 °C, pH = 3.0; N11: T = 55 °C, pH = 4.0.

phosphoric acid as an N-stabilising agent increased the phosphate content in the concentrate and consequently, the N:P ratio changed from <10:1 to 1:1.3 at pH 2.5. At pH 4 the N:P ratio was 1:2.5. The ammonium losses to the permeate were quite low in the phase 1 and phase 2, except for in run N7 where the losses were most probably due to wetting issues caused by preceding runs at pH 6. In phase 2, the ammonium losses to the permeate were quite low. 1.4 and 5.5 mg/L of ammonium were found in the permeate after the runs at pH 3.0 and 4.0, respectively. Based on these results, pH 4 was chosen for phase 3 because the ammonium losses were not drastically higher than at lower pH, and this implied limited use of acid. The temperature 55 °C was retained as the chosen temperature, due to a balance between reasonable permeate flux and evaporation losses.

3.2. Phase 3

Fig. 5 shows the permeate flux and ammonium concentration in the permeate over time. The flux decreased over time due to the deposition of particles on the membrane. The membrane was cleaned according to the procedure described in the supplementary material (S2) when the flux decreased to a fifth of the initial flux. At that time, the volume left in the boiler had been reduced by 80 % down to 20 L. After the cleaning process, the pre-experiments with tap water showed an increase in the permeate flux from 0.243 to 4.64 L/m^2h, being even higher than the pre-experiments before the experiment. The permeate conductivity of this tap water pre-experiment was 34 μS/cm, which was considered as an acceptable recovery of the hydrophobicity (<50 μS/cm), according to the manufacturer.

When the concentration process continued after cleaning the flux decline was steeper, which is shown by the linear regression lines in

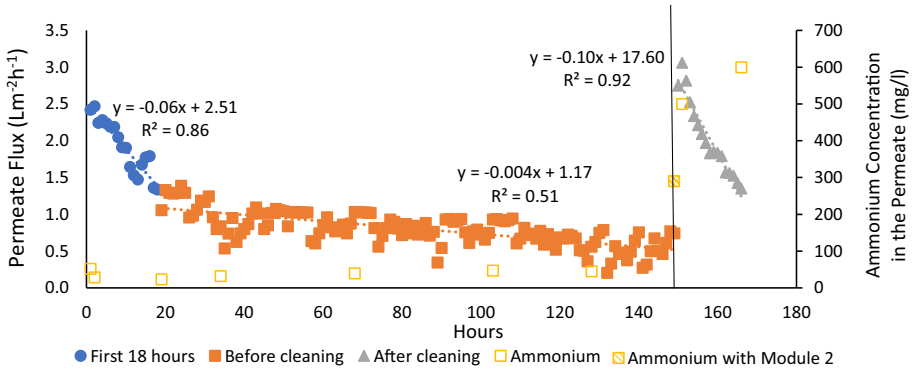

Fig. 5. Permeate flux and ammonium concentration in the permeate over time of experiment phase 3. The vertical line represents the hour of operation of Module 2. Before and after cleaning, Module 1 was operated.

Fig. 5. This could be explained by a higher concentration of particles in concentrate at the end of the experiment. This increase of solids contributed to membrane scaling and resulting in a more pronounced decrease of the permeate flux.

The conductivity measurements in the permeate during phase 3 (Table 4) indicated wetting of the membrane which became more pronounced during the end of the experiment. This also increased the ammonium concentration over time in the permeate. After membrane cleaning the flux was recovered, however the conductivity and ammonium concentration in the permeate were even higher than before the membrane cleaning. Possibly the concentrate at this time was too harsh for the membrane. For instance, in the permeates P8 (operated with new Module 2), P9 and P10 (shown in Table 4) non-volatile compounds like chloride, phosphate and sulphate were found, suggesting that these high concentrations caused wetting of the membranes quickly. This could be also observed in the loss of selectivity of phosphate, shown in Table 4. This indicates that at these operation conditions with very high concentrations of substances, there was a limitation in keeping the hydrophobicity of the membrane [25].

The ammonium concentration in the permeate phase 3 was higher in the first sample, compared to all permeate samples during phase 2. This may be explained by the blackwater digestate batch used for the phase 3, in which acetate was found. The presence of fatty acids could have affected the hydrophobicity of the membrane and caused wetting [26]. During phase 3, a large share of the water in the blackwater digestate evaporated into the air. Of the initial digestate volume of 100 L, only 43.5 L ended up in the permeate flux. This was due to the long duration of the experiment and the absence of sealing, resulting from the need to use an external tank.

3.3. Quality of the concentrate

The concentration of macro- and micronutrients, as well as problematic substances, after phase 3 are shown in Table 5. Most of the nitrogen was found in the form of ammonium, 93–95 % of phosphorous was in the form of phosphate and one-third of the sulphur was in the form of sulphate. Most of the metals were found mainly in dissolved form, except copper of which 25 % was in particulate form combined with organic matter. The weight/weight ratio of NPK in the concentrate was 1:3:0.3, where most of the phosphorous originated from the addition of phosphoric acid. In this experiment, nearly 33 % of the ammonium was lost while the loss of phosphorus was around 35 %, leading to the conclusion that most of the nitrogen losses resulted from wetting and were not due to the volatilisation of ammonia.

3.4. Chemical modelling

The model output of total and dissolved metals was a reasonable fit to the experimental data, although no analysis was performed for the oxidation state.

3.4.1. Feed

The theoretical chemical speciation of the metals in the blackwater digestate feed was studied based on simulations with increasing pH

Table 5
The concentration of nutritional and problematic elements in the concentrate.

Macro-nutrients		Micro-nutrients		Problematic Substances	
(mg/L)		(µg/L)		(µg/L)	
N	11,200	B	6820	As	145
P	25,600	Cu	1410	Pb	9.67
K	2630	Fe	1370	Cd	0.59
Ca	494	Mn	407	Hg	<1
Mg	248	Mo	65.5	Na	$3040*10^3$
S	196	Zn	1080	Cl	$5150*10^3$

Table 4
Permeate quality during phase 3. The concentrations of phosphate of P1 to P7 were measured in a composite sample.

Permeate sample	Module	Collection time (h)	Volume (mL)	NH_4-N (mg/L)	PO_4-P (mg/L)	Conductivity (µS/cm)	pH
P1	1	1	1020	52	57	570	4.74
P2	1	17	10,332	29	57	303	4.53
P3	1	15	6176	23	57	268	4.54
P4	1	34	9534	32	57	365	5.22
P5	1	27	5776	40	57	434	4.79
P6	1	25	5598	47	57	495	4.33
P7	1	22	3708	45	57	546	3.92
P8	2	1	1006	290	472	2920	3.80
P9	1[a]	1	1444	500	1240	4720	4.72
P10	1[a]	14	10,284	600	1470	5640	4.10

[a] Indicates after cleaning.

values. The simulated solid formation fitted the experimental concentrations of particulate metals in the feed. Hydroxyapatite, strengite, struvite, and gibbsite were considered to be the main mineral phases occurring in the model. The analysed concentration of DOC was 180 mg/l in the feed. It is most likely that the DOC corresponded to simple organic molecules or inert organic matter that did not interact with ions at this concentration because no interaction between organic matter and ions was observed. This fact, together with the limitations of the software meant that the organic matter was not considered in the model titration. Fig. 6a indicates that the formation of struvite is favoured at pH values above 6.6, while gibbsite and hydroxyapatite are formed up to pH values of 6.40 and 5.29, respectively. However, at pH 8.5 the highest modelled concentrations of struvite and hydroxyapatite were 75.6 mg/kg and 81 mg/kg, respectively. The measured pH was 7.7–7.8 in the blackwater digestate (Table 1). At pH 4, the only precipitates found in the model were carbonates with a total concentration of 1.92E-7 mg/kg as CO_3^{2-}. This suggests that mineral precipitation in the feed at the beginning of the concentration process should not contribute to any major scaling formation.

In the model at pH 9, 9.9 % of the ammonium was precipitated, while 89 % of the phosphate and 83 % of the magnesium were precipitated, due to the formation of struvite. On the other hand, the equilibrium speciation of ammonium and ammonia depends on pH and temperature. Most of the nitrogen was in the form of ammonium but was likely to be transformed into ammonia, potentially being lost into the air or permeate. The chemical speciation was simulated to improve the understanding of the behaviour of ammonium-ammonia in the digestate. The results indicated that the ammonia losses seen in the experiments may be related to the partial pressure of ammonia shown in Fig. 6 b. The simulated ammonia partial pressure under equilibrium conditions increased with system pH and temperature. Equilibrium was not reached during the membrane-distillation concentration process and the pressure inside the system was not atmospheric. The temperature difference reduces the pressure in the boundary layer of the membrane. The behaviour of ammonia was modelled at two different partial pressures. 0.15 atm was selected because water evaporates at 40 °C at 0.15 atm, as shown in Fig. 6b. This shows that the reduction in pressure does not significantly affect the ammonia losses.

3.4.2. Concentrate

The chemical speciation of the metals in the concentrate generated from phase 3 was simulated. The pH measured in the concentrate was 3.8. The mineral formation in relation to pH, and the concentrations of the various compounds in the concentrate were different to the equivalent values in the digestate.

According to the model simulations, 87 % of the phosphorus in the concentrate was dissolved, while the observed phosphate concentration was 93–95 % of the total phosphorus. The chemical equilibrium model simulations showed that only 0.17 % of the phosphate precipitated, while the chemical analysis showed around 2 % was precipitated. Table 6 shows the modelled solid minerals formation in the concentrate, where $CaHPO_4$, variscite and chloropyromorphite were the main phosphate solids potentially occurring. The model also showed that >88 % of the dissolved phosphate was in the form of phosphoric acid or its dissociated forms. The remaining phosphorus was in chemical species of phosphorus with magnesium, calcium, sodium, and potassium.

The concentration of different elements such as Mn, Si and Co that precipitated in the concentrate during the phase 3 matched the values found in the simulations. On the other hand, according to the chemical analyses, almost one-third of the sulphur in the concentrate was in the form of sulphate. The rest of the sulphur was simulated as being in the three oxidation states S(-II), S(0), and S(IV). Each type of sulphur

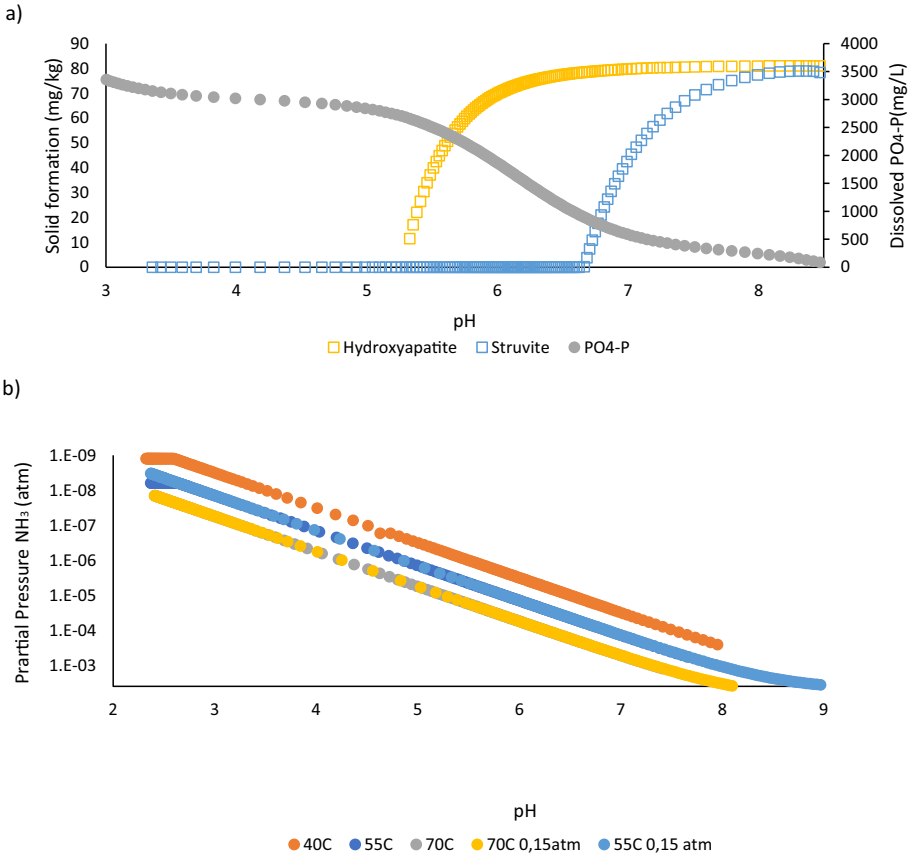

Fig. 6. Chemical model titration performed on blackwater digestate shows a) precipitates and phosphate concentrations and b) partial pressure of ammonia at different temperatures under different atmospheric pressures.

Table 6
Solid minerals at pH 3.8 and 25 °C, and gases formed in the concentrate according to Visual MINTEQ simulations.

Solid minerals	Concentration (mg/kg)		
Quartz	165.25		
$CaHPO_4$(s)	380.97		
Variscite	5.15		
Bixbyite	0.98		
$Co(OH)_3$(s)	5.60E-03		
Chloropyromorphite(c)	8.86E-03		
Gas	Partial pressure (atm)		
The oxidation state of S	S(+IV)	S(-II)	S(0)
SO_2 (g)	5.06E-05	7.24E-19	7.24E-19
H_2S (g)	1.20E-15	8.41E-02	1.20E-15

compound results in the formation of different gases. The partial pressures of CO_2 and NH_3 were independent of the oxidation state of sulphur and were 3.80E-04 atm and 3.81E-08 atm, respectively. Table 6 shows the partial pressures of SO_2 and H_2S if all of the sulphur not forming sulphate were to be in oxidation state S(IV), S(-II) or S(0). Those gases are harmful to human health and to the environment. According to the simulations, at oxidation state S(-II), the partial pressure of H_2S can reach 8.41E-02 atm, which requires further investigation.

4. Discussion

4.1. Permeate flux in the membrane distillation process, scaling and wetting

In general, when the concentration of ions in water increases, the heat capacity and boiling point increase, and the partial pressure of water vapour decreases. This was observed in the phase 3. After the membrane cleaning, the flux decreased faster than at the beginning of the experiment (Fig. 5 Permeate flux and ammonium concentration in the permeate over time of experiment phase 3. This implies that more heat was required to evaporate the water in the concentrate. These physicochemical phenomena occur because of the interaction of the water molecules with the dissolved ions. Additionally, in MD there are effects of concentration and temperature polarisation occurring in the boundary layer between the membrane and the liquid, which directly affect the permeate flux [16]. Those effects may be intensified by the increase in concentration.

Although a higher temperature increases the permeate flux in MD processes it also increases the scaling and decreases the cleaning efficiency [27]. Therefore, the biggest flux changes were observed after runs at 70 °C in the phase 1(Fig. 3a). The scaling blocks the pores and increases thermal resistance to decrease the permeate flux. Temperature also affects the ammonia-ammonium equilibrium: higher temperature leads to higher concentrations of ammonia dissolved in the digestate [28]. The ammonium-ammonia equilibrium does not seem to be significantly influenced by a lower atmospheric pressure (Fig. 6b), Therefore, is seems probable that the pressure difference generated by MD also did not have much influence on the ammonia losses. Another factor that influences the ammonia-ammonium equilibrium is the system pH. The system pH value also affects the formation of solid phases, as shown by the chemical equilibrium model simulations (Fig. 6a). In this study, the model simulations also showed that lower pH values (below 4) not only keep the ammonium on the blackwater digestate side but may also prevent solid deposits on the membrane.

The temperature difference between the hot and cold sides is one of the driving forces for increasing permeate flux in the membrane distillation process. Due to scaling, as shown in Fig. 3b, the permeate flux progressively decreased independent of the working temperatures. When the concentration of solids increased, it also increased the speed of scaling. Generally, MD can increase the concentration of the major components until a saturation point. The effect of concentration polarisation may have been a key factor in flux decline during the MD concentration processes, meaning a higher concentration of ions on the boundary layer of the membrane, with increasing scaling and wetting [26]. Another possible cause of wetting in the phase 3 could be organic fouling, which could produce forces attractive to other hydrophobic molecules [26].

In addition to this, an important component in the blackwater digestate is carbonates with an alkalinity above 5000 mg/L. These high concentrations may promote the formation of calcium carbonate, a compound that aggregates on polymeric membranes during MD [29]. However, the chemical model simulations showed that for the experiments carried out at pH 4 or below, most carbonates and bicarbonates were mainly present as carbon dioxide.

Improved pre-treatment, such as ultrafiltration, could improve the permeate flux and reduce scaling, which has been shown to increase the flux in an MD process for raw blackwater treatment [30]. Nanofiltration could also be considered, not just to improve the permeate flux but also to remove micropollutants, especially pharmaceuticals, and volatile fatty acids in the concentrate [31]. A permeate flux model with phase 1 and phase 3 using the equation of Liu et al. (1998) [32]. For Phase 3, the coefficient (β) associated with blackwater concentration was estimated across various volume reduction factors. It was observed that the estimation of β after cleaning was lower than the values before cleaning. This translates to a higher permeate flux, even though the concentrations of the black different solutes of blackwater digestate are higher [33], which may be an additional indication of wetting.

Also, the membrane type could be chosen to prevent wetting, which was the main problem associated with the process in the present study. Typical membrane types worthy of consideration are superhydrophobic, omniphobic [34], and two-faced membranes, also referred to as Janus membranes [35].

4.2. Nitrogen stabilisation

Phosphoric acid was added to the blackwater digestate for ammonium stabilisation, but at the same time this increased the concentration of phosphorous in the digestate, which was initially between 75 and 160 mg/L, even lower than the potassium concentration. After adding phosphoric acid, the concentration of phosphorus was almost three times higher than that of nitrogen, which increases the fertilizer potential value of the concentrate. However, phosphoric acid is rather expensive, and the acid also influenced the metal analyses which then had to be carried out with an adapted method because of the high phosphorus concentrations.

Nitrification could be used as a sustainable alternative nitrogen stabilisation solution. The high alkalinity and ammonium concentrations would be good sources of carbon and energy for nitrifying bacteria and archaea [36]. If nitrification could not transform all of the ammonia, some phosphoric acid could still be added to retain the ammonium in the concentrate.

4.3. Plant-nutritional and harmful aspects of the concentrate

The essential elements for plants are defined as macronutrients, which include nitrogen, phosphorous, potassium, sulphur, magnesium, and calcium, as well as micronutrients such as copper, iron, zinc, manganese, and boron, while other non-essential elements like selenium, silicon, and sodium can enhance plant growth [8]. The concentrated blackwater digestate contained all of the primary and secondary macronutrients and micronutrients (Table 5), which demonstrates the enormous potential of blackwater as a complete fertilizer, although 60 % of the phosphorus present came from the addition of phosphoric acid.

The mineral in the concentrate (Table 6) shows the formation of mineral phosphates that may be more difficult for plants to obtain, while the formation of gibbsite may be favourable since aluminium is less available for plants.

The blackwater digestate contains micronutrients that are required worldwide in agricultural soils. The lack of micronutrients could lead to a deficiency of micronutrients in humans [8]. Comparing the concentrate obtained with other digestates commonly used as fertilisers shown in Table 7, the concentrate obtained is quite rich in macronutrients and micronutrients. Macronutrients in the blackwater are in a similar range as the other digestate concentrates, but for Zn and Cu the blackwater concentrations are much lower. For all of the digestate compared, Hg was under detection limit for all digestate,. For As, Cd and Pb the membrane distillation concentrate and the dairy manure digestate are under the limits establish by the European Union (Table 7).

The blackwater concentrate contains substances that could potentially harm soil health and crops, including problematic elements such as As, Cd, Pb, and Hg (as indicated in Table 5). Another area of concern is sodium chloride, which is excreted in urine. The global population is currently consuming roughly twice the recommended amount of salt [40] and the accumulation of sodium chloride poses a significant challenge for agriculture on a global scale [41], although, in Sweden, highly soluble compounds find their way back to the sea through groundwater. Depending on soil and crop characteristics and applicable legislation it may be necessary to dilute the concentrate before use to avoid adverse effects to the environment.

Nevertheless, if we establish a nutrient and sanitation loop where human nutrition becomes intricately connected to soil nutrition, it then becomes imperative to reduce salt consumption. This reduction is crucial not only for human health but also for maintaining soil health.

4.4. Consequences of gas formation

According to the chemical model simulations, H_2S or SO_2 may be formed in the final blackwater concentrate at 25C. H_2S is usually present in blackwater digestate, as during anaerobic digestion sulphur-containing compounds (e.g. proteins) are degraded and H_2S is formed. H_2S and SO_2 have characteristic odours (although H_2S is odourless at high concentrations), which were not observed, neither during the phase 3 nor from the final product of phase 3. This may be explained in that the sulphur present was associated with organic matter. However, to be able to understand the gas formation better, more investigation is needed.

Table 7
Comparison between blackwater digestate concentrate, liquid fraction of pig slurry, energy crops digestate, and dairy manure digestate. EU regulation on limits of heavy metals for organic fertilisers.

Element	Unit	Membrane distillation concentrate	Pig slurry + liquid fraction of pig slurry and energetic crops [37]	Dairy manure digestate [38]	EU organic fertilizer limits [39]
N	gkg^{-1} DM	83.8	119–121	16.3	
P	g/kgDM	25.6	14.7–24.7	11.6	
K	gkg^{-1} DM	19.7		47.1	
Ca	gkg^{-1} DM	0.2		20.6	
Mg	gkg^{-1} DM	3.7		13.9	
Fe	$mgkg^{-1}$ DM	10.5		1448.8	
Cu	$mgkg^{-1}$ DM	11.2	37.1–87.5	51.2	
Zn	$mgkg^{-1}$ DM	8.1	109–325	275.3	
As	$mgkg^{-1}$ DM	1.1		4.7	40.0
Cd	$mgkg^{-1}$ DM	0.0	0.6–1.4	0.6	1.5
Pb	$mgkg^{-1}$ DM	0.1	1.4	7.2	120.0

4.5. Potential use for the permeate

One of the goals of this concentration process was that most of the volume ends up in the permeate, which could be a valuable by-product. Drinking water in the European Union must comply with a maximum concentration of 0.5 mg/L of ammonium [42]. Values below this limit were not achieved during the experiments of this study, not even in the phase 1 at pH 2.5. Nevertheless, the permeate may typically be suitable for irrigation, landscaping and other agricultural purposes.

The content of nutrients and problematic substances were found in similar ratios in the permeate to those found in in the concentrate but 5–300 times more diluted than in the concentrate depending on the permeate samples under consideration, because the quality of the permeate changed over time. fi<.

5. Conclusions

Blackwater digestate liquid contains macro- and micronutrients essential for plant growth. The concentration of blackwater digestate liquid using a membrane distillation process was shown to have great potential, but improvements have to be considered to mitigate membrane wetting. The experiments on air gap membrane distillation for the concentration of blackwater digestate under different pH and temperature values suggested that the most feasible operation parameters were a temperature of 55 °C and a pH of 4. Therefore, phase 3 was performed under these conditions achieving a volume reduction of 15 times. The concentrate obtained was rich in macro- and micronutrients, containing a weight-proportional NPK ratio of 1:3:0.3. The high P content present in the concentrate was due to the use of phosphoric acid for ammonium stabilisation. The low concentrations of problematic metals and metalloids are lower the European regulation organic fertilizer limits [39]. The chemical equilibrium model simulations showed the potential formation of solids such as $CaHPO_4$(s), strengite and bixbyite and also the possible interaction of particulate organic carbon with some of the micronutrients such as copper, thus reducing its availability for plants.

CRediT authorship contribution statement

Stephanie Rusch Fehrmann: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Annelie Hedström:** Writing – original draft, Supervision, Resources, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Elisabeth Kvarnström:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Juan Antelo:** Writing – review & editing, Supervision, Software, Data curation, Conceptualization. **Iemke Bisschops:** Writing – review & editing, Validation, Supervision, Conceptualization. **Inga Herrmann:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

We, the authors of the research manuscript " Nutrient concentration of blackwater digestate using an air gap membrane distillation process " declare that we have no conflicts of interest about the research project. The funding for this research has been provided by governmental agencies, ensuring impartiality and transparency in our findings and conclusions.

We affirm that our involvement in this research is driven by the pursuit of scientific inquiry and the advancement of knowledge in our

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2024.106357.

Data availability

Data will be made available on request.

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