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Ammonia recovery from pig slurry using a membrane contactor-Influence of slurry pretreatment

Agata Zarebska[1] (*), Henrik Karring[1], Morten Lykkegaard Christensen[2], Maibritt Hjorth[3], Knud Villy Christensen[1], Birgir Norddahl[1]

[1] Department of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Niels Bohrs Allé 1, DK-5230 Odense M, Denmark

[2] Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Sohngaardsholmsvej 57, DK-9000 Aalborg, Denmark

[3] Department of Engineering, Aarhus University, Blichers Allé 20, Postboks 50, DK-8830 Tjele, Denmark

* Corresponding author. Tel.: +45 52631110. E-mail address: agata.agnieszka.zarebska@gmail.com (A. Zarebska)

Abstract

Pig slurry contain sufficient amount of nitrogen, phosphorus, and potassium for plant growth. Appropriately administered this could substitute significant amounts of fertilizer. However, excessive fertilization with slurry causes environmental problems. To reduce environmental issues, solid-liquid separation or anaerobic digestion is needed to obtain a better distribution of nutrients. Solid-liquid separation produces a solid fraction rich in phosphorus and a liquid fraction containing ammonia, potassium, and a high water content. Therefore, further concentration of ammonia is desired for any practical use. In this study ammonia membrane stripping was carried out using polypropylene membranes and the impact of temperature, flow velocities and liquid fraction pretreatment on the membrane contactor performance was tested. Sieved liquid effluents from a decanter centrifuge, a screw press, an AL-2 system (flocculation and filtration) and an anaerobic digester were tested. Since the properties of these liquid effluents vary they might affect ammonia recovery. Thus it is essential to investigate which effluent is most suitable as a feed for a membrane contactor and what is the cost of preprocessing. The mean ammonia mass transfer coefficient at 30°C was found to be equal to $17\pm2 \cdot 10^{-3}$ $m \cdot h^{-1}$. At 50°C it was found to be equal to $29\pm2 \cdot 10^{-3}$ $m \cdot h^{-1}$ for all the tested effluents. This means that sieving after slurry separation or anaerobic digestion alleviates the influence the solid-liquid separation has on ammonia membrane stripping. However, the cost evaluation showed that solid-liquid separation using a decanter centrifuge followed by sieve draining is the cheapest of the methods investigated.

Keywords: animal slurry, membrane contactor, ammonia recovery, mechanical separators, anaerobic digestion

List of symbols and abbreviations

A_{filter}	filter area (m^2)
A_m	membrane area (m^2)
A_{sieve}	laboratory sieve filter area (m^2)
AL-2 system	commercial flocculation and filtration system for solid-liquid slurry separation (AL-2 Teknik A/S, Hovborg, Denmark).
C_f	concentration of solids in the feed effluent ($kg \cdot m^{-3}$)
$C_{TAN}(t)$	TAN concentration at time t ($g \cdot l^{-1}$)
C_{TAN0}	TAN concentration at time zero (Initial effluent feed concentration in a membrane stripping experiment) ($g \cdot l^{-1}$)
DM	dry matter
Ei	collected liquid slurry effluents. i: 1-5 refers to different farms and pretreatments as shown in Fig. 1.
Ei*	collected liquid slurry effluents sieved through a 125 µm aperture sieve. i: 1-5 refers to different farms and pretreatments as shown in Fig. 1.
Ei**	collected liquid slurry effluents sieved through a 125 µm aperture sieve. i: 1-5 refers to different farms and pretreatments as shown in Fig. 1.
g	gravitational acceleration constant ($m \cdot s^{-2}$)
$h_t(t)$	actual suspension level at time t (m)
K_m	overall mass transfer coefficient ($m \cdot s^{-1}$)
L	length of active filter area on belt filter (m)
M	total sample mass in sieving experiment (kg)
PP	polypropylene
R_m	filter medium resistance (m^{-1})
SDS-PAGE	sodium dodecyl sulfate-polyacrylamide gel electrophoresis
t	time (s)
t_1	beginning time at which sieving experiment starts (s)

TAN	total ammoniacal nitrogen
TKN	total Kjeldahl nitrogen
TS	total solids
V_f	initial sample volume of feed for the membrane stripping experiment (m^3)
VS	volatile solids
$V_{filtrate}/t$	rate of filtrate production ($m^3 \cdot s^{-1}$)
α	specific cake resistance ($m \cdot kg^{-1}$)
Δp	hydrostatic pressure difference across filter (Pa)
η	filtrate viscosity (Pa·s)
ρ	filtrate density ($kg \cdot m^{-3}$)
χ	experimental constant defined as $\chi=(\rho \cdot g)/(\eta \cdot \alpha \cdot (M/A_{sieve}))$

1. Introduction

Livestock manure is a complex mixture of urine, faeces and water. This slurry contain nutrients such as nitrogen, phosphorus, and potassium, which are valuable for plant growth. If these nutrients are separated and administered correctly, nutrients derived from slurry has the potential to compete successfully with mineral fertilizers (Bouwman et al. 2009). Unfortunately the dramatic increase in animal production over the last decades has not always been followed by proper slurry management. This has led to increased ecosystem pollution as nutrients from animal wastes are released into the environment (De Vries et al. 2012; Westerman and Bicudo 2005). These problems are further enhanced by the fact, that most animal production is concentrated in areas far from the fields where the fertilizer is needed (Halberg et al. 1995; Nielsen and Kristensen 2005). To circumvent these problems and reduce transport costs, processing techniques involving solid-liquid separation e.g. screw pressing or decanter centrifuging of the slurry, or anaerobic digestion combined with solid-liquid separation is often used (De Vries et al. 2012; Sørensen and Thomsen 2005). Slurry processing though affects the slurry's physical and chemical properties (Hjorth et al. 2010). During anaerobic digestion, microorganisms degrade organic matter. This release sugars from carbohydrates, fatty acids from lipids, and amino acids from proteins. The amino acids are further degraded which increase the ammoniacal nitrogen content in the effluent (Batstone et al. 2002; Burton and Turner 2003). Digestion causes dry matter (DM) reduction and change the particle size distribution in the digestate (Hjorth et al. 2010; Masse et al. 2005). Solid-liquid separation

reduces the phosphate and organic content in the liquid fraction of the slurry and digestate. However, with solid-liquid separation it seems only possible to remove 15 - 45% of the nitrogen from the liquid fraction (Hjorth et al. 2010).

Though relatively low, the concentration of nitrogen in the liquid fraction is still too high for the liquid fraction to be safely discharged to the environment. Therefore, further separation to increase the nitrogen concentration is crucial for almost any practical fertilizer application and to obtain a liquid fraction that can be discharged to the environment or reused for cleaning in the animal production (Foged 2011). Membrane stripping is one of the useful methods for removing and concentrating volatile ammonia from the liquid fraction of animal slurry (du Preez et al. 2005; Waeger-Baumann and Fuchs 2012). Among the operating conditions tested, pH, temperature and feed velocity have the largest influence on the ammonia removal process. Increasing the pH and temperature has a positive effect on ammonia mass transfer (du Preez et al. 2005; Waeger-Baumann and Fuchs 2012) while the ammonia mass transfer decreases at low feed flow velocities due to increased mass transfer resistance (Semmens et al. 1990). In order to use membrane contactors successfully though, the slurry liquid fraction has to be sieved first. If sieving is not performed, the channels of the membrane modules will be blocked irreversibly over time. The combined influence of solid-liquid slurry separation methods and sieving on membrane contactor performance has so far not been investigated, nor has the economic costs of these separation stages been evaluated.

This study therefore evaluates the combined influence of different solid-liquid slurry separation methods and sieving as a pretreatment of liquid slurry before the membrane contactor (Fig.1). It further includes an economic cost evaluation of the proposed processes.

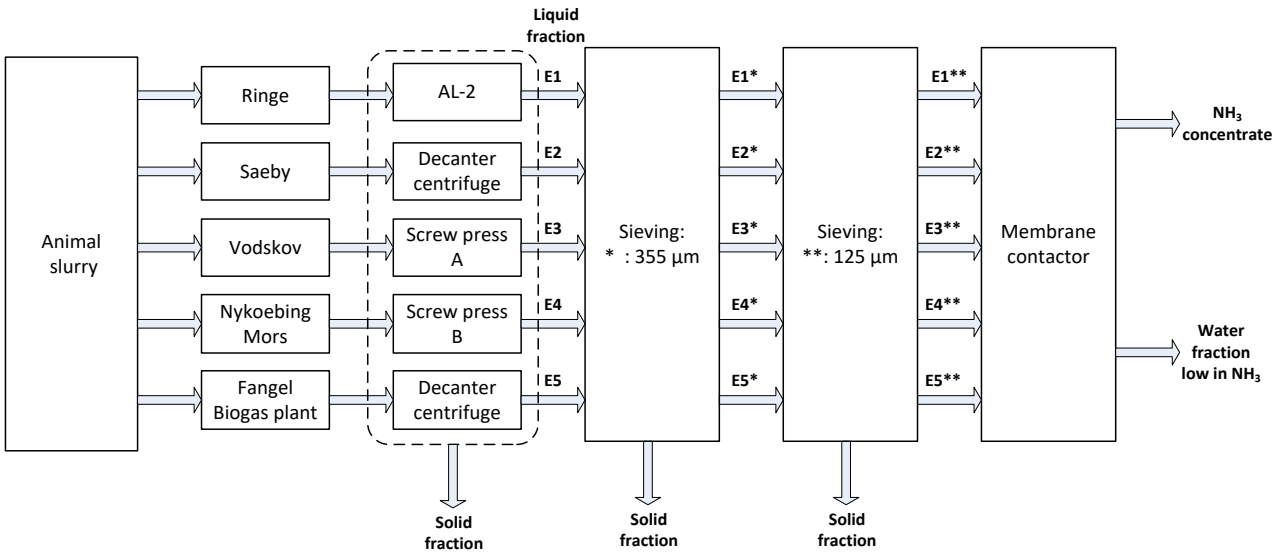

Fig. 1 Schematic representation of the different slurry effluents and solid-liquid separation steps tested as preprocessing steps to ammonia membrane stripping

The study specifically test the influence of sieving on membrane contactor for ammonia removal at different temperatures (30°C and 50°C) and feed flow velocities (0.9 $m \cdot s^{-1}$ and 1.8 $m \cdot s^{-1}$) using pig slurry liquid effluents from three different types of separation units: a decanter centrifuge, a screw press and an AL-2 system (flocculation combined with a gravity belt filter followed by a screw press). For comparison a decanter centrifuged biogas digestate is included in the tests.

2. Materials and methods

2.1. Slurry

Liquid slurry effluents were collected from four different Danish pig farms located in Ringe, Saeby, Vodskov and Nykoebing Mors, respectively, and for comparison, digestate from one Danish biogas plant in Fangel. The farms use different solid-liquid separation techniques to produce the slurry liquid fraction effluents as shown in Fig. 1. Effluent 1 (E1) was collected from an AL-2 system (flocculation combined with a gravity belt filter followed by a screw press), effluent 2 (E2) from a decanter centrifuge, effluent 3 (E3) from a screw press A, effluent 4 (E4) from another screw press B, and effluent 5 (E5) from a decanter centrifuge at the biogas plant.

2.2. Gravity draining

To avoid larger particles blocking the membrane tubes, all liquid slurry effluents have to be sieved. In the laboratory experiments this was done by consecutive sieving through sieves (Retsch 5657- W. Germany DIN 4188) with apertures of 355 µm (effluents E1*-E5*) and 125 µm (effluents E1**-E5**), as indicated in Fig. 1. In order to estimate the cost of sieving in full farm or process scale prior to membrane stripping, a series of gravitational draining tests were performed using samples of approximately 420 mL. The draining setup consisted of a transparent glass cylinder with a height of 21.5 cm and a diameter of 5 cm placed on the sieves mentioned above. The samples were placed in the cylinders and allowed to drain by gravitation. The collected filtrate mass was continuously logged by an analytical balance. The filtrate viscosity was measured in duplicate with a Bohlin Instrument CV 120, UK. The mass of the filter cake was determined as the difference in the content of dry matter (DM) in the feed and the filtrate. The flow resistance from the sieves could be neglected due to their relatively large aperture.

2.3. Ammonia Membrane contactor

A schematic representation of the membrane contactor setup used for ammonia removal is depicted in Fig. 2. To avoid ammonia loss to the surroundings the setup was constructed as two closed systems: An alkalized effluent system from

which the ammonia was stripped and an acidified absorber system into which the ammonia was absorbed in the form of ammonium. In this way the membrane contactor formed the only path through which ammonia could escape the effluent. The membrane used was a tubular polypropylene membrane (PP, MD020TP N) from Microdyn Nadir. Sieved liquid slurry was passed through the membrane lumen side, while the sulfuric acid 0.5 M (VWR A/S Herlev, Denmark) was pumped into the shell side in countercurrent flow. The pH of the sieved pig slurry was adjusted to 11 using 5 M NaOH (prepared using deionized water and NaOH pellets, 99% pure from VWR A/S Herlev, Denmark). The effluents E1**-E3** required 46±6 ml of 5 M NaOH per 1L of slurry effluent while the effluents E4**-E5** required 103±16 ml of 5 M NaOH per liter of slurry effluent. Both sieved slurry and acid solutions were recycled to their respective tanks.

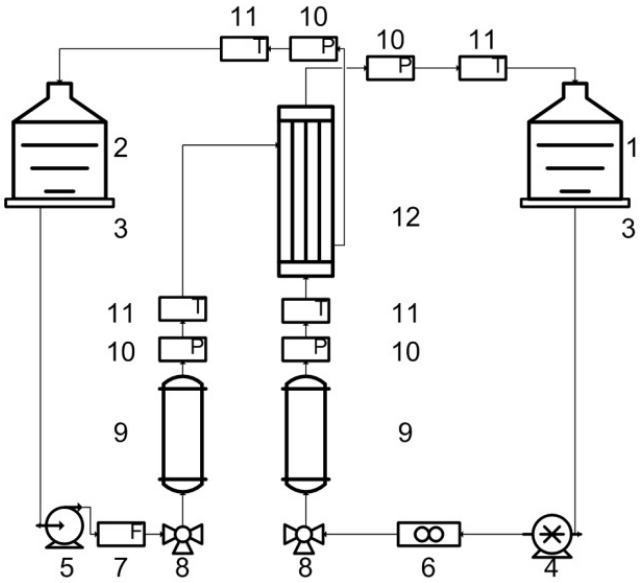

Fig. 2 The membrane contactor experimental set-up: 1: feed reservoir; 2: acid reservoir; 3: balances; 4: membrane pump; 5: centrifugal pump; 6: IFC 100 Krohne Mag flowmeter; 7: Platon Bobbin flowmeter, 8: 3-way valves; 9: heat exchangers; 10: pressure gauges; 11: thermometers; 12: PP membrane

Samples were taken from the feed and acidic stripping solutions at regular time intervals during the experiments. On the feed side the ammonia concentration was determined using a standard Kjeldahl distillation unit (Kjeltec TM2100, Höganäs, Sweden) and back titration (APHA Standard Method 2005). The same procedure was used on the acidic shell side except for experiments using E1**, E2**, and E3** as feed. In the latter case the ammonium concentration on the acidic shell side was determined by Dr. Hach-Lange ammonium kits (LCK 303 (2-47 mg/L), Hach-Lange GmbH, Dusseldorf, Germany) and a digital spectrophotometer Dr 2800.

157 2.4. Liquid slurry sample composition

158 The particle size distributions were measured in triplicate using a Mastersizer 2000, Malvern Instruments (Malvern
159 Instruments Ltd, Worcestershire, UK). Prior to characterizing the chemical composition of supernatants (colloids and
160 dissolved matter) and removed solids (particles), the effluents were centrifuged at 5000 rpm for 30 min. Dry matter and
161 volatile solids were determined gravimetrically after heating at 105°C for 24 h and 550°C for 1 h, respectively (APHA
162 Standard method 2005, 2540 B and 2540 E).

163 Total Kjeldahl nitrogen (TKN=Organic-N+NH_3-N+NH_4^+-N) of both solids and supernatants was determined using a
164 Foss Tecator TM Digester Auto (Höganäs, Sweden) through destruction by 15 ml of sulphuric acid 98% (Merck,
165 Darmstadt, Germany) using 2 Kjeltabs CK as catalyst (3.5 g Potassium Sulphate K_2SO_4, 0.4 g Copper (II)
166 Sulphate·$5H_2O$, Foss Tecator AB, Höganäs, Sweden). Quantification was done using the APHA Standard Method
167 2005, 4500-Norg B. Afterwards total ammoniacal nitrogen (TAN) in supernatants was determined according to APHA
168 Standard Method 2005, 4500-NH_3 B using a Kjeltec TM2100, Höganäs, Sweden. The protein content was determined
169 based on the assumption that almost all the nitrogen is present in amino acids/proteins or as TAN. Thus the protein
170 content of the liquid slurry samples were calculated by subtracting the TAN from the TKN values before multiplying
171 with the general nitrogen to protein conversion factor of 6.25. In addition, the protein composition of the liquid fraction
172 (supernatant) and solid fraction of the different effluents before and after sieving were characterized by sodium dodecyl
173 sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) under reducing conditions and using the SDS-PAGE Buffer
174 System (Laemmli 1970). Briefly described, the effluent samples were diluted in ultrapure water and centrifuged at
175 16,160 *g* for 5 minutes to separate liquid and solids. The supernatants (liquid fractions) were transferred to new tubes
176 while the water-insoluble pellets were thoroughly washed in ultrapure water. Subsequently, the fraction samples were
177 mixed with SDS-PAGE sample buffer containing a final concentration of 5 mM dithiothreitol. SDS-PAGE was
178 performed using hand-cast 4-16% gradient gels (7.3 cm × 8.3 cm × 1 mm). The proteins were then visualized by
179 Coomassie Brilliant Blue staining.

180 2.5. Data analysis

181 2.5.1. Specific cake resistance

182 The specific cake resistance was determined based on the draining experiments. Based on a plot of the suspension level
183 in the cylinder versus time, the period of pure filtration before consolidation or blocking was identified (Christensen et
184 al. 2010).

The linearized form of equation 1 (see appendix B1 in Electronic Supplementary Material for more details) was then used to determine the specific cake resistance during pure filtration. The standard deviation of the specific cake resistances was estimated based on the 95% confidence interval of the slope (χ). An example showing how the specific cake resistance is calculated is presented in appendix B2 in Electronic Supplementary Material.

$$h_t(t) = h_t(t_1) \cdot e^{-\chi \cdot (t - t_1)} \quad \text{Eq.1}$$

Where

$$\chi = \frac{\rho \cdot g}{\eta \cdot \alpha \cdot \frac{M}{A_{sieve}}}$$

If the settling velocity is fast compared with the draining rate, the amount of cake is constant during the draining process. The settling rate depends on the size and density of the individual particles. Because of the broad particle size distribution in the slurry effluent it is not possible to determine the settling rate of the particles. Instead the settling velocity is classified as fast or slow compared to the draining velocity based on visual inspection. This introduces a rather qualitative element into the procedure. However if, as a worst case scenario, the settling velocity is zero, the correct specific cake resistance will be 50% higher than the calculated value.

2.5.2. Filter area

To estimate the extra costs of the required draining, the required filter area for a full-scale continuous belt filter was calculated based on the measured specific cake resistance and equation 2 (McCabe et al. 2001). As mentioned the true resistance is equal to 1-1.5 of the estimated resistance. Both extremes were used in equation 2 to estimate the filter area.

$$\frac{\frac{V_{filtrate}}{t}}{A_{filtrate}} = \frac{\sqrt{\frac{2 \cdot \alpha \cdot \Delta p \cdot C_f}{t \cdot \eta + \left(\frac{Rm}{t}\right)^2}} - \frac{Rm}{t}}{C_f \cdot \alpha} \quad \text{Eq.2}$$

The following assumptions were made to evaluate the process feasibility using continuous belt filtration, a typical belt width of 2 m, belt velocity of 2 m·min^{-1}, and filtrate production of 10 m^3·h^{-1} (DB 2013). The hydrostatic pressure exerted by the liquid was calculated assuming a 5 cm suspension height on the filter belt (Werner 2013).

2.5.3. Ammonia mass transfer

The overall mass transfer coefficient (K_m) was determined from the change in TAN concentration with time (du Preez et al. 2005).

$$\ln\left(\frac{C_{TAN_0}}{C_{TAN_{(t)}}}\right) = \frac{K_M \cdot A_M}{V_f} \cdot t \qquad \text{Eq. 3}$$

By plotting $\ln\left(\frac{C_{TAN_0}}{C_{TAN_{(t)}}}\right)$ against time a straight line with a slope of $\frac{K_M \cdot A_M}{V_f}$ is obtained. The overall mass transfer coefficient is found from this slope together with the standard deviation of the slope within a 95% confidence interval.

3. Results and discussion

3.1. Gravitational draining

3.1.1. Influence of slurry characteristics on gravitational draining

Both the particle size distribution and the chemical composition of the slurry could be expected to affect filtration and membrane contactor performance. These properties will depend on animal breed, size, gender, diet composition, and slurry treatment (Masse et al. 2005). In addition pig slurry is a very heterogeneous mixture, thus particle size, physical properties and chemical composition might show large variations due to the sampling procedure (Christensen et al. 2009). Therefore, to evaluate the draining and membrane contactor performance the physical properties and chemical composition of the five slurry liquid fractions were analyzed.

The particle size distribution (Fig. A2, A3 and A4 in Electronic Supplementary Material) of the effluents E2, E3 and E4 are bimodal, as opposed to the effluents E1 and E5 (Fig. A1 and A5 in Electronic Supplementary Material) which have unimodal distributions. Further the anaerobically digested effluent E5 show a lower particle size with particle diameters distributed between 1 and 125 µm. This is characteristic for digested manure (E5) as the microbial process degrades organic particulate matter. The particle size distribution affects significantly the filtration. Depending on the filter aperture size, larger particles will be deposited on the filter, whereas smaller particles will either pass through the filter or be partly retained by the filter cake. As the smaller particles starts to close the filter cake channels, these are blocked and the filtering process slows down. A broad particle size distribution thus leads to a denser filter cake and slower draining. Based on the measured particle distributions, it is concluded that for effluents E1, E2, E4, and E5 gravitational draining remove particles above 125 µm. For effluent E3, sieving did not remove particles above 1 mm in size. This suggests post agglomeration of smaller particles in the filtrate after sieving, rather than an analytical experimental error, since the characteristic bimodal size distribution is also seen before sieving.

The characteristic properties of the slurries are shown in Table 1. The total solids content in the unsieved slurries varied from 15.0 $g \cdot kg^{-1}$ for an AL-2 effluent to 54.1 $g \cdot kg^{-1}$ for a decanter centrifuge effluent. The unsieved decanter centrifuge

effluent (E2) has higher dry matter content (54.1 g·kg^{-1}) than the screw press effluents E3 and E4 (30.0 g·kg^{-1} and 31.3 g·kg^{-1}, respectively). After sieving through a 355 µm aperture filter, the total content of the solids dropped to between 7.5 - 53.8 g·kg^{-1}. Sieving through a 125 µm aperture filter reduced the dry matter content to between 7.4 - 25.8 g·kg^{-1}. Particles capable of passing the 125 µm aperture sieve represented 40 - 50% of the total content of solids in the slurry effluents E1, E2 and E4, and 69% and 80% in the case of effluents E3 and E5, respectively. Effluents E3 and E5 has a higher content of smaller particles than effluents E1, E2 and E4. This should result in a denser filter cake structure. Effluents E3 and E5 is therefore expected to show a slower gravitational draining than effluents E1, E2 and E4.

3.1.2. Determination of the specific cake resistance

The observed differences in the particle size distributions (Appendix A in Electronic Supplementary Material) for the slurries will affect the sieving processes. This could be expected to affect the properties of the sieved liquid slurry effluents and as a consequence, could have an impact on the membrane ammonia stripping process.

The draining process can be divided into three stages (Christensen et al. 2010):

Stage 1: Cake formation, when particles settle and form the filter cake

Stage 2: Pure filtration, when liquid is filtered through a filter cake of constant size

Stage 3: Cake collapse, when the filter cake compresses

The transition between pure filtration and cake collapse is observed as an abrupt change in the draining rate. For some of the draining experiments (E3, E4, and E5) the draining almost stopped (Fig. 3b and 3d). This is probably a consequence of filter cake channel blocking or filter aperture blocking by smaller particles. Further, based on visual observations during the experiments and based on Fig. 3a-3d, the settling velocity is high, hence stage 1 can be neglected. Therefore the cake resistance can be calculated using equation 1.

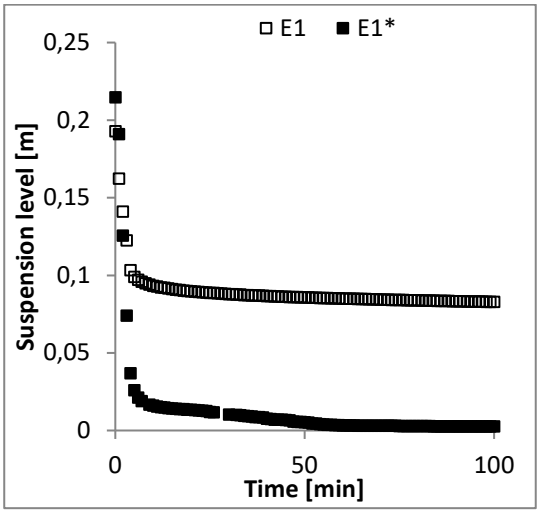

Fig. 3a Draining of AL-2 effluent through 355 µm (E1) and 125 µm sieve (E1*)

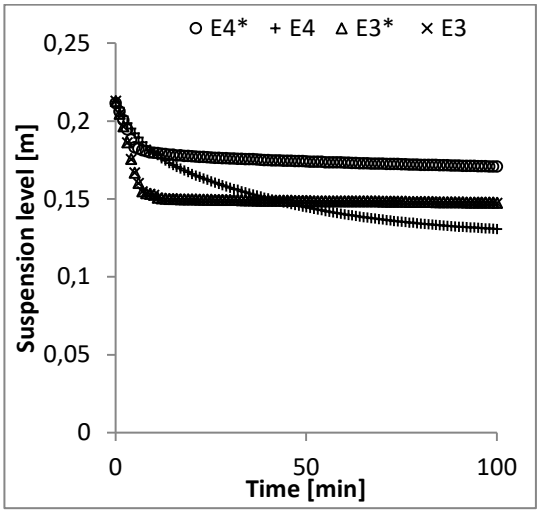

Fig. 3b Draining of screw press effluents A & B through 355 µm (E3, E4) and 125 µm sieve (E3*, E4*)

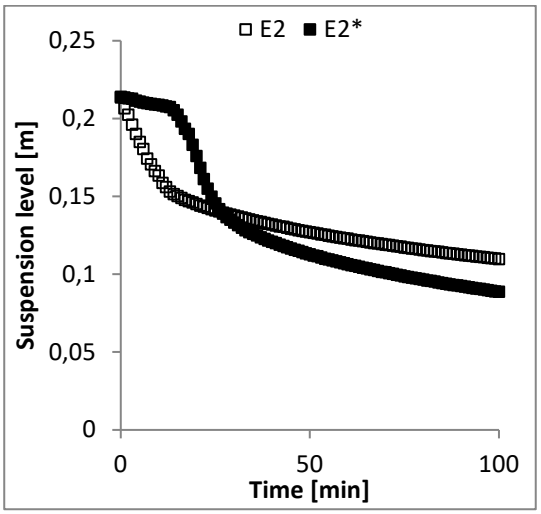

Fig. 3c Draining of decanter centrifuge effluent through 355 µm (E2) and 125 µm sieve (E2*)

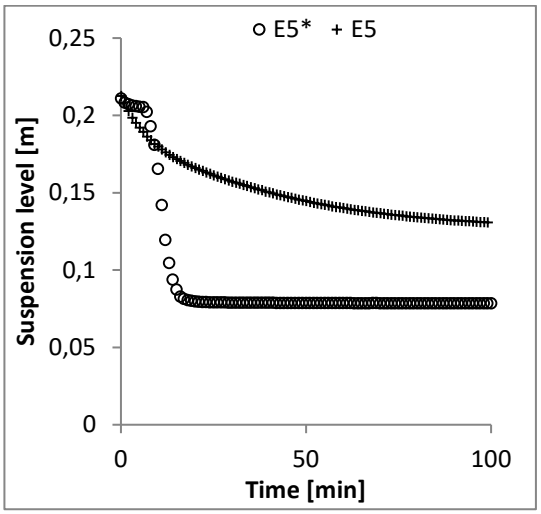

Fig. 3d Draining of anaerobically digested effluent separated by decanter centrifuge through 355 µm (E5) and 125 µm sieve (E5*)

The cake resistance decreases with cake porosity (McCabe et al. 2001) and the resistance increases with the specific surface area of the particles. The specific surface increases quadratically with decreasing particle size. The specific resistance is therefore high for small particles and should increase with decreasing sieve aperture. As seen from Table 1 this is indeed the case except for effluent E2. A relatively low cake resistance is observed for E2. Sieving with aperture 125 µm though is associated with a high standard deviation. This may explain why the cake resistance obtained with the 355 µm sieve seems higher for this effluent.

The findings are in accordance with the results of Hjorth et al. (2010); Karr and Keinath (1978). They found that supracolloidal particles in the range of 1 to 100 µm produce filter cakes of higher resistance, thus making filtration slower, compared to more porous cake structures containing particles and substances like hairs.

Both particle size distribution and gravitational draining curves for the E1 and E2 effluents presented on Fig. A1, A2 in Electronic Supplementary Material and Fig. 3a, and 3c show a change from pure filtration to consolidation. This indicates a relatively easy gravitational draining.

Based on the gravitational draining data and particle size analysis for effluents E3 and E4 (Fig. 3b, Fig. A3, Fig. A4 in Electronic Supplementary Material) blocking of the filter cake channels or filter aperture is a problem. Further, particles around 50 – 100 µm are collected in the filter media or cake when draining through a 125 µm sieve. This is in agreement with Karr and Keinath (1978) observations that particle size distribution has a large influence on the specific cake resistance. In the case of effluent E5 specific cake resistance values are not similar for aperture 355 µm and 125 µm, although they have similar particle size distributions. Based on the draining data (Fig. 3d) and particle analysis (Fig. A5 in Electronic Supplementary Material), it is suggested that effluent E5 has a higher content of supracolloidal solids. This increase cake channel and sieve aperture blocking (Karr and Keinath 1978). For E5, the anaerobically digested effluent, the filter cake channel or aperture blocking is not as critical as for the screw press effluents (E3 and E4). Moreover the previous effluent treatment history is also important. For instance AL-2 effluent E1, with the lowest amount of particles, and decanter centrifuge effluent E2 with the highest, are relatively easy to drain, when compared to screw press effluents (E3 and E4) and anaerobically digested effluent separated by decanter centrifuge (E5). Even though both decanter centrifuge effluent E2 and screw press effluents E3 and E4 contained large particles, only in the latter case could these large particles retain small particles leading to blocking of the filter cake channels and sieve apertures. For E1 flocculation using flocculants had been carried out prior to the belt filtration and screw press

296 separations. It is therefore possible that small particles likely to adhere to larger particles (flocs) had mainly been
297 removed in the stages prior to the gravitational draining. This would lead to less severe filter cake channel and sieve
298 aperture blocking at the draining stage.
299 For the screw press effluents E3 and E4 filter cake channel and sieve aperture blocking seems to present a serious
300 problem. For these cases a different separation method therefore has to be considered.
301 3.1.3. Cost estimate for a full scale draining filter
302 To implement the sieve draining at the farm scale level, a belt filter unit has to be added between the solid-liquid
303 separation step and the membrane contactor unit. In order to estimate the added cost of purchasing a belt filter unit, the
304 filtration area of the belt filter was determined from the specific cake resistances (Table 1). The costs of the belt filters
305 were estimated based on information in Peters et al. (2004). The calculated filtration area for treatment of the different
306 effluents including the purchase costs of sieve apertures are shown in Table 2. It is seen that the purchase cost of the
307 belt filter with an aperture of 355 µm increase as E4 < E1 < E2 < E5 < E3, while for an aperture of 125 µm the order is:
308 E2 < E1 < E4 < E3 < E5. In this case, for both screw press effluents (E3** and E4**) and anaerobically digested
309 effluent (E5**), the high cost of filtration is due to filter cake channel and sieve aperture blocking, which obstructs the
310 filtration. It is further noticed (Table 2) that the extra expenses incurred by using flocculants during the solid-liquid
311 separation might be partly returned by the reduced filtration area in the sieving step (E1 compared to E3). Thus removal
312 of fine particles prior to the sieving step could be beneficial, if the 125 µm aperture size is chosen.
313 3.2. Membrane ammonia stripping
314 3.2.1. Influence of the feed slurry characteristics on membrane contactor
315 The main problem when using membrane contactor is membrane fouling and wetting. Fouling slows down the mass
316 transfer and wetting changes the process from ammonia stripping to simple microfiltration (Zarebska et al. 2014).
317 Among the many compounds present in the slurry liquid fraction, such as inorganics, humic substances, carbohydrates
318 and lipids, the most problematic foulants for membrane contactor operation are proteins (Wang et al. 2009; Zarebska et
319 al. 2014). Fouling induced by protein adsorption changes the membrane hydrophobicity leading to membrane wetting.
320 Therefore the protein content and the molecular weight of the proteins in the effluent fractions have been determined,
321 while no attempt was made in the present study to measure inorganic compounds, carbohydrates, humic substances and
322 lipids. Unsieved slurry and slurry sieved through a sieve with an aperture of 125 µm were separated into solid and
323 liquid fractions by centrifugation in order to determine their protein content. It was found that for effluents E1-E4
324 volatile organic solids represent 25 - 50% of the total solids (Table 1). Except for E5 and E5** where 100% and 69% of

325 total solids were found to be volatile suspended solids, respectively, this is in agreement with the results of Moller et al.
326 (2002). The total Kjeldahl nitrogen content bound to both solid and liquid fractions after centrifugation was determined
327 for both unsieved and sieved slurry. By comparing total Kjeldahl nitrogen values before sieving with those after
328 gravitational draining it is found that 2 - 29% of the total Kjeldahl nitrogen content was associated with particles. Of
329 these approximately 16 - 31% originated from proteins or peptides (Table 1). Additionally, pretreatment by draining
330 reduced the protein content with 25 - 32% in the case of effluents E1, E2, E3, and 59% and 41% for effluents E4 and
331 E5, respectively. The total ammoniacal nitrogen in the supernatant account for more than 80% of total Kjeldahl nitrogen
332 for all effluents, except for E2 and E2**, where total ammoniacal nitrogen represent only 4% and 16% of total Kjeldahl
333 nitrogen, respectively. The results show, that among undigested slurry, E3** and E4** effluents have the lowest
334 protein/amino acids content, namely 1.20 $g \cdot L^{-1}$ and 1.21 $g \cdot L^{-1}$, respectively. The molecular weight of the proteins of the
335 liquid fractions determined by SDS-PAGE revealed significant differences between the effluents (E1 - E5; Appendix C
336 in Electronic Supplementary Material). No proteins were detected in the liquid fractions of the sieved and unsieved E1
337 and E2 effluents, while the fractions of sieved and unsieved effluents E3 - E5 showed faint and smeared staining for
338 proteins. Smear in protein gels is often caused by too high salt concentrations in the sample, proteolytic degradation of
339 the proteins, or some posttranslational modifications which cause protein bands to smear. Therefore, to further analyze
340 the effluents, the protein fractions extracted from the solid fractions were also investigated (Appendix C in Electronic
341 Supplementary Material). The solid fractions of sieved and unsieved effluents E1 and E2 revealed no protein lanes. The
342 effluents E3 - E5 on the other hand showed significant “smearing” with a few relatively distinct protein bands. These
343 bands migrate with molecular weights in the range of 25 - 60 kDa and a distinct band about 100 kDa. According to the
344 staining intensities it appears that especially for E3 the concentration of proteins in the solid fraction is reduced upon
345 sieving (E versus E** fractions). Despite that the effluent solids were washed with water to remove excess salts prior to
346 the SDS-PAGE analysis the smear did not disappear. Further the smear was observed for all protein bands. This
347 suggests that the smear is caused by degradation of proteins. The partly degraded proteins in the sieved and unsieved
348 effluents E3, E4, and E5 indicate protein denaturation. This exposes the hydrophobic regions in the degraded proteins
349 and leads to increased interaction between the degraded proteins and the membrane surface. For long term operations
350 without membrane cleaning this will lead to membrane fouling with consecutive wetting (Zarebska et al, 2014). In order
351 to prevent fouling, protein should be removed prior to membrane contactors. Based on previously published study
352 (Zarebska et al., 2015), it was found that protein removal is a key to successful operation of membrane contactors.
353 Ammonia mass transfer was quadrapled as a result of removing some of the proteins by MF and some by UF.

3.2.2. Effect of temperature and feed flow velocity upon ammonia removal

The effect of temperature and feed flow velocity on the mass transfer of ammonia was investigated using the sieved effluents E1**, E2** and E3** as feed. The observed overall mass transfer coefficients were at 30°C: With a cross flow velocity of 0.9 $m \cdot s^{-1}$, for E1** $15 \pm 4 \cdot 10^{-3}$ $m \cdot h^{-1}$, for E2**$17 \pm 2 \cdot 10^{-3}$ $m \cdot h^{-1}$and for E3** $17 \pm 5 \cdot 10^{-3}$ $m \cdot h^{-1}$; With a cross flow velocity of 1.8 $m \cdot s^{-1}$, for E1** $19 \pm 2 \cdot 10^{-3}$ $m \cdot h^{-1}$, for E2**$18 \pm 3 \cdot 10^{-3}$ $m \cdot h^{-1}$ and E3**$16 \pm 5 \cdot 10^{-3}$ $m \cdot h^{-1}$. The observed mass transfer coefficients are identical within the estimated 95% confidence intervals. This indicates that sieving levels out any influence the prior solid-liquid separation has on the ammonia stripping process. Further the results are in agreement with Semmens et al. (1990). They too found, that doubling the feed solution velocity from 0.9 $m \cdot s^{-1}$ to 1.8 $m \cdot s^{-1}$ has a negligible effect on the mass transfer. Based on their findings and the present study, it can therefore be concluded, that neither concentration polarization nor temperature polarizations have a measurable influence on ammonia mass transfer under the conditions investigated. When the feed temperature was increased to 50°C the mass transfer coefficients increased: for E1** to $28 \pm 4 \cdot 10^{-3}$ $m \cdot h^{-1}$, for E2** to $30 \pm 7 \cdot 10^{-3}$ $m \cdot h^{-1}$ and for E3** to $30 \pm 2 \cdot 10^{-3}$ $m \cdot h^{-1}$, all measured at a cross flow velocity of 1.8 $m \cdot s^{-1}$. Thus, increasing the temperature from 30°C to 50°C increases the overall mass transfer coefficient with a factor of about 2, with no significant difference observed between the different slurry effluents. The positive influence of temperature observed in the present study is in agreement with du Preez et al. (2005) who for ultrafiltrated slurry reported an overall mass transfer coefficient of $24.9 \cdot 10^{-3}$ $m \cdot h^{-1}$ at 25°C and of $62.1 \cdot 10^{-3}$ $m \cdot h^{-1}$ at 55°C. The obtained lower ammonia mass transfer coefficients in the present study might be caused by the higher membrane thickness employed, as the mass transfer coefficient is inversely proportional to the membrane thickness. In addition, the values reported by du Preez et al. (2005) are four times as high as those found by Ahn et al. (2011). For PTFE membranes Ahn et al. (2011) reported mass transfer coefficients between $5.4 \cdot 10^{-3}$ $m \cdot h^{-1}$ and $7 \cdot 10^{-3}$ $m \cdot h^{-1}$ depending on the suspended solid content. This inhibitory effect of the suspended solids on the overall ammonia mass transfer was found to be as important as a temperature increase from 22 °C to 35 °C, but less important than the influence of pH, feed and absorbent flow rates. This is similar to the results found for PTFE membranes by Zarebska et al (2015). For a model manure solution they found that a particle free solution had a mass transfer coefficient of $64 \cdot 10^{-3}$ $m \cdot h^{-1}$, while for a model manure solution with particles sieved through a 125 µm mesh a mass transfer coefficient of $28 \cdot 10^{-3}$ $m \cdot h^{-1}$ was found. When they tested a PP membrane with the same model manure solutions, no such dependence on particle content was seen. This could indicate that for PP membranes solid particle content is of little influence. In the present study a PP tubular membrane was used, using slurries with different dry matter content, but with similar particle size distributions. Thus based on the slurry experiments alone the influence of particle size distribution cannot

be judged. Therefore, as biogas digestate is known to have a particle size distribution different from that of undigested slurry, the sieved liquid fraction from centrifuged digestate and centrifuged undigested slurry was tested as well. Again it was observed that the mass transfer coefficients within the experimental 95% confidence limits were identical, for E4** $18.9\pm0.9\cdot10^{-3}$ $m\cdot h^{-1}$ and for E5** $19\pm1\cdot10^{-3}$ $m\cdot h^{-1}$ at 40°C. Thus all of this lead to the conclusion that after sieving the overall mass transfer coefficient of ammonia through PP membranes was not influenced significantly by the presence of particles. This is in contrary to what has been found for PTFE membranes as reported by Ahn et al. (2011) and Zarebska et al. (2015). The significance of these results are that when planning a process, for ammonia removal from liquid slurry by membrane ammonia stripping, the solid-liquid separation process has no influence on the ammonia stripping process as long as sieving is performed prior to membrane stripping as long as PP membranes are used.

4. Conclusions

The following conclusions can be drawn from the experimental results:

1. Sieving is beneficial to ammonia recovery by stripping when using a membrane contactor. It reduces the risk of blocking the membrane tubes, removes any influence the solid-liquid separation could have on the overall ammonia mass transfer during membrane contactor operation and increases the mass transfer rate.
2. No significant difference in membrane distillation performance was found between slurry effluents with similar particle size distribution but different dry matter content.
3. Increasing the membrane contactor operation temperature from 30°C to 50°C doubled the overall mass transfer coefficient of ammonia.
4. Increasing the membrane contactor feed flow rate beyond 0.9 m/s had negligible effect on the measured overall mass transfer of ammonia.

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Table 1 Manure characterization before and after sieving

Effluent	Density ($kg \cdot m^{-3}$)		Total solids ($g \cdot kg^{-1}$)		Cake resistance ($m \cdot kg^{-1}$)		Viscosity ($Pa \cdot s$)		M (g)	Solid								Liquid								Total
										TS ($g \cdot kg^{-1}$)		VS ($g \cdot kg^{-1}$)		TKN wet ($g \cdot kg^{-1}$)		Protein ($g \cdot kg^{-1}$)		TKN ($g \cdot L^{-1}$)		TAN ($g \cdot L^{-1}$)		Protein + Amino acids ($g \cdot L^{-1}$)		TKN ($g \cdot L^{-1}$)		Percentage of TKN associated to particles (%)
	Mean	SD	Mean	SD	Mean	SD	Mean $\cdot 10^{-3}$	SD	Mean	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
E1	1003	2	15.0	0.4						7.8	0.3	3.4	0.1	7.7	0.7	0.29	0.05	2.02	0.04	1.76	0.01	1.59	0.4	2.1	0.1	3
E1*	995	3	7.5	0.2	$9 \cdot 10^{8}$	$3 \cdot 10^{8}$	3.6	$7 \cdot 10^{-2}$	3.8																	
E1**	992	2	7.4	0.1	$2 \cdot 10^{9}$	$1 \cdot 10^{8}$	3.5	$3 \cdot 10^{-2}$	0.1	6.5	0.3	2.65	0.07	6.2	0.7	0.21	0.05	1.26	0.01	1.03	0.01	1.39	0.02	1.30	0.06	3
E2	1034	4	54.1	0.2						51	1	16	2	1	3.9	0.4	1.3	0.2	0.52	0.02	0.02	0.01	3.11	0.02	0.7	0.2	29
E2*	1025	5	53.8	0.8	$4 \cdot 10^{8}$	$2 \cdot 10^{7}$	3.5	0.1	4.8																	
E2**	1009	4	21.9	0.5	$1 \cdot 10^{8}$	$4 \cdot 10^{7}$	3.5	$1 \cdot 10^{-2}$	17.5	49.9	0.5	12.9	0.6	3.1	0.1	0.98	0.06	0.48	0.04	0.08	0.01	2.50	0.04	0.6	0.1	25
E3	997	3	30.0	0.1						19.7	0.4	10.0	0.1	13.5	0.3	1.29	0.09	3.71	0.03	3.41	0.05	1.85	0.06	3.98	0.09	7
E3*	995	1	28.6	0.5	$3.0 \cdot 10^{9}$	$1 \cdot 10^{7}$	4.0	$9 \cdot 10^{-2}$	8.7																	
					$3.2 \cdot 10^{9}$	$2 \cdot 10^{7}$																				
E3**	998	2	20.9	1.3	$3.1 \cdot 10^{9}$	$2 \cdot 10^{7}$	3.8	$7 \cdot 10^{-4}$	9.3	17.3	0.4	8.5	0.3	10.8	3	0.04	0.87	0.04	3.1	0.2	2.99	0.04	1.2	0.2	3.4	0.2	6
E4	1028	9	31.3	0.5						14.5	0.5	5.9	0.3	13.2	0.6	0.8	0.1	4.58	0.01	4.22	0.07	2.28	0.07	4.8	0.1	4
E4*	1004	4	18.0	1.1	$1 \cdot 10^{8}$	$9 \cdot 10^{6}$	3.6	0.1	6.3																	
E4**	1000	2	14.4	0.1	$1 \cdot 10^{9}$	$6 \cdot 10^{7}$	3.7	$8 \cdot 10^{-2}$	6.1	11.9	0.4	5.3	0.6	8.67	0.03	0.34	0.01	4.45	0.09	4.25	0.01	1.21	0.09	4.55	0.09	2
E5	1005	3	32.1	0.5						13.5	0.4	13.8	0.1	13.8	0.9	0.8	0.1	5.0	0.1	4.38	0.03	3.8	0.1	5.2	0.3	4
E5*	998	3	30.3	0.2	$4 \cdot 10^{8}$	$2 \cdot 10^{7}$	5.3	$4 \cdot 10^{-2}$	2.9																	
E5**	998	2	25.8	0.6	$6 \cdot 10^{9}$	$5 \cdot 10^{8}$	5.3	$4 \cdot 10^{-2}$	3.4	13	2	9.4	0.4	9.3	0.6	0.5	0.1	4.51	0.04	3.85	0.06	4.13	0.07	4.6	0.1	3

[*] Effluent sieved with aperture 355µm, [**] Effluent sieved with aperture 125µm, [(#)] Based on one measurement due to insufficient amount of effluent

476 **Table 2** Cost estimation of continuous belt filtration of liquid manure effluents

Effluent	A (m^2)	L (m)	Δp (Pa)	Cost ($)
E1*	5.8	2.9	488.1	90 000
E1**	5.0	2.5	486.4	60 000
E2*	9.0	4.5	502.8	100 000
E2**	1.1	0.6	495.0	20 000
E3*	42.5	21.2	487.8	200 000
E3**	39.4	19.7	489.4	200 000
E4*	1.7	0.8	492.5	40 000
E4**	11.2	5.6	490.6	100 000
E5*	9.0	4.5	489.4	100 000
E5**	109.3	54.6	489.3	300 000

477 * Effluent sieved with aperture 355 µm, ** Effluent sieved with aperture 125 µm

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