Ammonium Fertilizers Production from Manure

A Critical Review

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Abstract

Excessive livestock production in small areas poses a risk of nitrogen release to the environment and thus air and water contamination. Recovery of ammonia is necessary to avoid overfertilization, but manure management of untreated slurry is costly and complex. The authors discuss ammonium fertilizer recovery from manure using membrane processes and physicochemical methods including technology and energy assessments. Currently, nanofiltration, reverse osmosis, membrane distillation combined with ultrafiltration, and air stripping are the best choices. The processes rely highly on selection of appropriate pretreatment, as residual particulates will lead to fouling of membranes and stripping towers hence affect the performance greatly.

Keywords: ammonia recovery, biofertilizers, slurry, membrane technology, physicochemical treatment

INTRODUCTION

Projections indicate that the world population of close to 7 billion will grow to 9.3 billion by 2050 *(1)*. The food production needs to increase over 2 per cent every year up to 2030 with doubling of current global production by 2050 to meet the demands of the larger population *(2, 3)*. As this increase in food production will have to occur on less arable land this can only be achieved by enhancing production *(4)*.

Nitrogen is one of the most essential plant nutrients, and is often the most important determinant of plant growth and crop yield *(5-7)*. Chemical fertilizers add N in readily available form to plants resulting in intensification of food production and increased yield.*(8)*. Commercial fertilizers are currently responsible for 40–60% of the world's food resources (9). However, only about half of the N-fertilizers are taken up by crops, while the other half is lost to the atmosphere as ammonia (NH_3), nitrogen oxides (NO_x), nitrous oxide (N_2O) or to aquatic systems, as nitrate (NO_3^-) (10). Ammonia and nitrogen oxides contribute to soil pollution via acid deposition,11 water pollution via eutrophication (12) and to global warming (13). Furthermore, increasing concentrations of N_2O in the atmosphere is responsible for ozone layer depletion (14). The estimated ammonia emission from N-fertilizer is equal to 10–12 million tons per year (15).

Livestock production is increasingly carried out on farms with relatively small land areas attached. This has resulted in excessive production of animal wastes that no longer can be applied sustainably in the region as fertilizer (16). Transport of nutrient surplus from the farm over long distances is hence necessary to avoid excess load of nutrients and to mitigate environmental problems. Problems associated with high costs of transport, loss of nutrients to the environment and over-fertilization can be partly solved by separating manure into a liquid fraction rich in inorganic N and potassium (K) and a solid fraction rich in phosphorus (P) (17). The solid fiber fraction can be used for instance as soil conditioner, as fertilizer on P-

deficient regions with few or no animals, as a substrate for biogas plants or for energy production by incineration (18–21). The liquid fraction from separated slurry has a high water content and low nutrient concentration. It is usually intended to be used on farmlands near animal production as a fast acting N-fertilizer with lower ammonia emission than raw slurry (18,22) However, the unbalanced production of animal waste in regions with too little demand of the nutrients calls for separation. The purpose of any further separation of the liquid fraction is to decrease its volume and concentrate N and K in easily transportable and usable fractions which can be sold and make a profit (23). Based on a Spanish market survey, an ammonium-sulfate solution with a nitrogen content of 6% w/w and low organic content could be sold at a price of 0.35 € kg⁻1 N, while the management cost of untreated slurry in the Netherlands is 4–9 € kg⁻1 N (21,22). Moreover, nitrogen pollution costs the European Union between 70 and 100 billion € per year, where agriculture contributes significantly to the reactive N runoff in water.24 As a consequence of environmental issues and for economic reasons, ammonia recovery from manure is necessary (25).

This review aims to support decision making on the reuse of manure ammonium as fertilizer. Therefore, we discuss critically different methods for ammonium fertilizer production from animal wastes and include a technology and energy assessment. For convenience of this paper the methods available for ammonia recovery are divided into membrane and physicochemical processes. The review paper covers research involving: air stripping (AS), steam stripping, chemical precipitation (CP), ion exchange (IE), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), and membrane distillation (MD). As these methods to a varying degree require removal of particulate matter, the review also includes pretreatment of manure using solid-liquid separation, chemical additions, and micro- (MF) and/or ultrafiltration (UF).

TECHNOLOGIES FOR MANURE PRETREATMENT
Solid-Liquid Separation
Before ammonia can be recovered from manure, the manure has to be separated in a solid fraction rich in P and a liquid fraction rich in N. The obtained liquid fraction should be low in dry matter in order to improve the ammonia recovery, as particulate solids lead to membrane fouling, clogging of air stripping towers and impede chemical precipitation or ion exchange.

Solid-liquid separation may be performed in sedimentation tanks, where the settled solids are removed from the bottom of the tank (22). Settling of particles can be reinforced by increasing the gravitational force, as done in decanter centrifuges (22). Alternatives for solids removal are mechanical filtration using screw presses or drainage through press or belt filters (22). In 2010, Hjorth et al. (22) and in 2013 Christensen et al. (26) reported extensive reviews of options for solid-liquid separation of animal slurries. Based on their studies, separation efficiency of mechanical separators for the removal of dry matter and N in descending order is as follows: centrifugation > sedimentation > nonpressurized filtration > pressurized filtration. Moreover, sedimentation is a relatively simple and cheap method for removing solids from manure (22). The duration of sedimentation is highly dependent on the initial dry matter content. The highest removal reported (60%) was obtained when initial dry matter was between 10–20 g·l⁻¹ (22). The particle removal efficiency of decanter centrifuges increases with dry matter content. Decanter centrifuges were found to be more successful in retaining particles of size larger than 20–25 μm in the solid fraction (22). Drainage in general is more efficient in separating cattle slurry than pig manure due to a higher fraction of larger particles in cattle manure. Drainage can be hindered by particles clogging the filter. This increases the specific filter resistance. This is especially the case for particles within the range of 1 and 100 μm (27) Most of the N is found in dissolved form or in particles below 125 μm in size. Thus, most of N will end up in the liquid effluent after drainage with some remaining in the wet filter cake (22). The application of pressure in a screw press or belt filter press enables more

of the liquid and small particles to pass through the filter. This leads to a decrease in N separation efficiency (22).

The Use of Coagulants and Flocculants
The efficiency of solid-liquid separation can be enhanced by addition of cations or polymers resulting in fine particles aggregation due to coagulation and/or flocculation(22,26). Flocculation will lead to production of a cleaner effluent which is desired before further ammonia recovery. At the same time though polymers will also increase the concentration of NH_4^+ retained in the flocs in the solid fraction (22). There are examples of full-scale solid-liquid separation plants combined with flocculation using polyacrylamide polymer (PAM) operated on pig farms in Spain, Italy, and the United States(28–30) and combinations of coagulation and flocculation on central manure separation plants in the Netherlands.(31,32). Martinez-Almela and Barrera(28) reported on the full-scale separation efficiency using the Ecopurin system. The Ecopurin system gave a reduction of 84–95% of total suspended solids (TSS) and 19–47% of NH_4^+ in the effluent. Even better results were reported by Vanotti et al.(30), obtaining 93% removal of TSS, 78% of chemical oxygen demand (COD) and losing only 4% of NH_4-N using also the Ecopurin solid-liquid separation module. Riano and Garcia-Gonzalez (29) tested a screw press combined with flocculation. They achieved the lowest separation efficiency, 68% removal of total solids (TS), 70% of COD, and 2% of NH_4-N. Foged (32) reported a 78% removal of TSS and a 22% retention of total ammoniacal nitrogen (TAN) after flocculation with PAM and filtration on a belt filter on the Kumac Mineralen plant (NL). However, flocculants have also lead to membrane fouling when effluent from solid-liquid separation with low suspended solids content is used as a feed. This suggests that surplus polymer remained in the liquid after flocculation.33 Hoeksma et al. (31) and Foged(32) reported that coagulation of the belt filter liquid fraction with $Fe_3(SO_4)_2$ followed by air flotation alleviates this problem to such an extent, that the liquid fraction can be applied to RO concentration. At Kumac Mineralen, the solid fraction is skimmed off during flotation. The liquid fraction is then subjected to depth filtration on a continuous paper filter. Though Hoeksma et al (31) does not include a depth filtration in their process description, a visit to Gebrüderen Verkoyen's manure separation plant in the Netherlands, confirms that this step is necessary before RO (34).
The use of chemical additives such as polymers and inorganic salts may though have a negative impact on the environment if the solid fraction is applied to soils as fertilizer (35).

Microfiltration
Studies on microfiltration of animal wastes focus on removal of suspended solids (SS), organic matter (OM), nitrogen and phosphorus from manure. Microfiltration of pig manure has been found unsuccessful (36) nevertheless it works well for sow manure (37) and piggery wastewater (38). A direct comparison of the experiments is difficult as the feed varies up to tenfold in TS. The operating conditions vary also. However, some general conclusions can still be drawn based on the work done so far. A summary of current studies on MF are presented in **Table 1**.

Table 1 Summary of experimental MF treatment of manure

Reference	Feed	Membrane	Operating condition	Cleaning methods	Permeate quality	Problems
Pieters et al. (37)	Filtered sow slurry: TS 15-20 g l^{-1}, pretreated with sedimentation and bag filter 100 μm	Ceramic membrane Aluminum oxide (Al_2O_3) (Sephi-Matic 184R) with membrane surface 3m^2 and pore size 0.1 μm	Pressure 1.7 bar, Concentration factor 5.1, Temp. influent 34°C, Temp. filtrate 51^{0}C, Mean flux 64.1 L m^{-2} h^{-1}	Back pulsing, every 229.5 sec for 0.5 sec	Only suspended solids has been removed, while the dissolved dry matter and nutrients content did not alter	NR
Lee et al. (38)	Piggery wastewater: SS 0.5-0.7 g L^{-1} and COD 5-6 gL^{-1} ,BOD 3-4 gL^{-1}, pretreatment: anaerobic effluent prefiltered by steel filter with pore size 63 μm with suspended solids	Mixed esters of cellulose (**MCE**) with pore size 0.5 μm	Flux 10-30 L m^{-2} h^{-1}	Air-backwashing every 10 min for 5 s, chemical cleaning after 50 days with 1 N NaOH and 1 N HCl	SS < 0.2 g L^{-1}, COD- 1-1.5 g L^{-1}, BOD 0.3-0.4 g L^{-1}	Inorganic and biofouling
Zitomer et al. (90)	Digested dairy cattle manure pretreated with 6.35 mm screen	Sintered Titanium (**Ti**) with pore size 0.2 μm, with diameter 19 mm and surface area 0.09 m^2	Flux 40-80 L m-2 h-1	Washing with 3.5% NaOH, followed by water and phosphoric acid 3%	NI	Abrasion
Karakashev et al. (36)	Pig manure, anaerobic reject from decanter centrifuge with TS 21 ±0.9 g L^{-1}, VS 16 ±1.03 g L^{-1}, COD 23 ±2.3 g L^{-1}	Capillary MRC SUR 2342, Mitsubishi, with membrane surface 1.5m^2 and element size 1.035 x 446 x 13 mm,	Aeration 30 L h^{-1}, max. flux 13.6 L m^{-2} h^{-1}	Back-flushing after few days	TS - 10.5 g L^{-1}, VS - 9.6 g L^{-1}, COD – 16.1 g L^{-1}	Foaming problem after 12h, and membrane fouling after 3-4 days
Gerardo et al. (143)	Digested dairy sludge, Pretreatment: sedimentation, screen 500μm TS: 11.9 g L^{-1} TSS: 2.11 g L^{-1}	Ceramic membrane (Membralox), pore size 0.2 μm, area 0.22 m^2	NI	NI	TS 2.60 g L^{-1}, TSS 1.48 g L^{-1}	NI

NI – No information, NR- Not reported, SS = suspended solids, VS = volatile solids, COD = chemical oxygen demand, BOD biological oxygen demand.

Prior to microfiltration, raw slurry is commonly first subjected to traditional separation units using chamber filter presses, vibrating screens, liquid cyclones, decanter centrifuges, or screw presses (37). However, additional prefiltration steps are necessary to avoid that sand and other particles clog or damage the membrane. Pieters et al. (37) applied 100 μm bag filters to increase membrane lifetime. Different pretreatment techniques have been used for effluents from anaerobic digesters like for instance decanter centrifuges (36) or stainless steel prefilters

(38). Lee et al. (38) reported that the best membrane performance was achieved with a 63 μm pore size prefilter.

The highest flux has been achieved using ceramic membranes, with mean flux equals 64.1 L m^{-2} h^{-1} at 34°C and 1.7 bar (37). The best permeate quality with the lowest SS, COD, and biological oxygen demand (BOD) was reached by mixed cellulose ester (MCE) membranes with a maximum flux of 38 $l·m^{-2}·h^{-1}$ at 20 °C (38). It may be explained by the material and filtrationproperties of cellulose esters. Cellulose esters have a high permeability toward water and low solubility toward the salts (39). Additionally, the ceramic membranes make use of screen filtration, whereas the cellulose esters work by depth filtration. Thus, in ceramic membranes particle size exclusion dominates, while when MCE membranes are used, particle adsorption initially dominates.

Ceramic membranes have advantages compared to polymeric membranes. They have a narrow pore size distribution, are easy to clean, tolerate a wider range of pH,40 and have longer expected lifetimes. Despite those advantages, inorganic membranes at present are not favorable economically compared to polymeric membranes. This is due to a much higher membrane cost (40). Because of the high fouling potential of the feed, frequent or unforeseen membrane replacement can be necessary. It is therefore important to use low cost membranes that have the lowest possible impact on the economic viability of the plant.

Ultrafiltration

A summary of current studies on UF is presented in Table 2.

Table 2 Summary of experimental UF treatment of manure

Reference	Feed	Membrane	Operating condition	Cleaning methods	Permeate quality	Problems
Pind et al. (42)	Digested cattle slurry: TS 24÷25 gL^{-1} pretreatment: rotating prefilter with pore size 60 μm and an effective area 25 cm^2	A/G-UFP-100-E-4A membrane Polysulfone (**PSU**) (A/G Technology Corporation) MWCO 100 kDa, area 420 cm^2	Pressure 0.8–0.9 bar, max. flux ~ 30 L m^{-2} h^{-1}	During first 64 h, every 15-18 h cleaning with hot water, back pulsing after 64.5 h, every 5-18 h	NI	NR
du Preez et al. (23)	Digested pig manure: TS 4%	Tubular (12 mm) Polysulfone (**PSU**) module from Weir-Envig Pty. Ltd., South Africa with a mean pore size of 40 kDa with a total membrane area of 1.7 m^2	Pressure: 5–6 bar, crossflow velocity 2 $m·s^{-1}$, Flux: ~10 $l·m^{-2}·h^{-1}$	Water flush HNO3 pH > 2, 1 h Water flush NaOH max. pH 10 1 h once a week Water flush, Enzyme protease Permeate flush 5 min/2h	No suspended Solids TS<10 $g·l^{-1}$	NI
Fugere et al. (52)	Pig manure pretreated with: 1) settling, 2) vacuum filtration, 3) sieving & settling, 4) sieving, biological treatment & settling	5-HFM-251-FNO (Koch membrane), Polyvinylidene fluoride (**PVDF**), MWCO 100 kDa, pore size 0.01 μm, area 0,1 m^2 flow 10-20 L m^{-2} h^{-1}, inner diameter 2 cm	Temperature 15-25°C, Pressure 1 bar, Concentration factor 2.1-9 Mean flux 15 - 20 L m^{-2} h^{-1}	Chemical cleaning with Koch Kleen soap 1wt% for 30÷60 min, mechanical cleaning with sponge ball, washing with water, to prevent bacterial growth, pH was raised to 10-10.5 and with 1N NaOH and 0.1% NaN_3	Removal of SS and bacteria, sCOD and P with N pass through the membrane through the membrane	Concentration polarization and cake layer formation

Zhang et al. (53)	Digested pig slurry	Tubular Polyethersulphone (**PES**) (Weir Envig, Paarl, South Africa), MWCO 20 kDa, inner diameter 12 mm, module 10 cm long	Pressure 0.2-0.7 bar Flux 100 L m^{-2} h^{-1}	Chemical cleaning after 135 days with 0.5% EDTA combined with 1% Na$_3$PO$_4$ or using HNO$_3$	NI	Inorganic fouling with residual organic foulants
Lopez-Fernandez et al. (46)	Digested swine manure with SST 1.247gL^{-1}, tCOD 1.978 gL^{-1}, sCOD 0.832 gL^{-1} prefiltered with 500 μm screen	Tubular Polyethersulfhone (**PES**) (Koch, CTG-HFM251), cut-off 100 kDa, filtration area 0.017 m^2 Hollow fiber polyvinylidene fluoride (**PVDF**) (ZW-1, GE process & technologies), pore size 0.04 μm, filtration area 0.93 m^2	Pressure 1.3 bar, Temperature 30°C, average flux 20 L m^{-2} h^{-1}	PES membrane: Chemical cleaning with a basic and a basic-hypochlorite (200mgL^{-1}) PVDF membrane: Chemical cleaning with NaClO (500mgL^{-1}) for 30 min and if necessary also with citric acid (1000mgL^{-1})	PES membrane, TS removal, COD removal 60-65% PVDF membrane 70-75%	NR
Konieczny et al. (44)	Ppig slurry: COD 3.8 g/L, BOD 2.9 g/L Pretreatment: Centrifugation	Polyvinylidene fluoride (**PVDF1**) (100 kDa), **PVDF2** (50kDa), Polyethersulphone **PES1**(10 kDa), **PES2** (5 kDa)	Pressure: PVDF1 :3 bar PVDF2: 3.5 bar, PES1: 4.5 bar, PES2: 5.0 bar	Washing with water for 30 min	PVDF1&PVDF2: COD removal 50%, BOD 50% PES1&PES2: 75%	Reversible & Irreversible Fouling

NR = not reported, tCOD = total chemical oxygen demand, sCOD = soluble chemical oxygen demand

These studies show that ultrafiltration is able to remove most of organic particles and suspended solids larger than approximately 100 kDa including bacteria. Similar to MF, ultrafiltration performance depends on the pretreatment methods. Fixed filters did not succeed in prefiltering digested cattle manure to a sufficient degree (41) whereas rotating filters with pore size of 60 μm efficiently removed suspended solids (42). To reduce fouling effects on the UF, removal of suspended solids or attempts to change physicochemical properties of raw pig manure, settling (ST), settling combined with sieving (SAS), settling combined with biological treatment and sieving (SB), vacuum filtration (VF), and centrifugation have been tested (43,44).

The largest flux decline was observed for pig manure, which was vacuum filtrated (600 μm), and the smallest change of flux with the highest permeate quality was achieved with sieved (500 μm), biologically treated, and settled supernatant (43). The flux decrease can be explained by two phenomena: polarization and cake layer formation. Better results obtained for settled and settled and sieved manure supernatant compared to vacuum filtrated effluent could be due to ageing and particle size. VF effluent contained bigger organic particles, while ST and SAS supernatants were composed of aerobically and anaerobically degraded organic matter. It is highly probable that the higher organic content resulted in greater fouling of the membrane observed as a sharp flux decrease. A sharp decrease of flux from 100 to 5 l·m^{-2}·h^{-1} was noticed after two months during separation of digested pig manure with a tubular polyethersulfone (PES) membrane (45). Also Lopez-Fernandez et al.[46] reported a 93% decrease in permeability using a PES membrane, while when using a polyvinylidene difluoride (PVDF) membrane only a 25% decrease was observed. This demonstrates that PVDF membranes are more fouling resistant. The pore size has also a significant effect on fouling as mentioned previously in relation to the filtration properties. Konieczny et al. (44) reported that a PVDF membrane with a molecular weight cutoff (MWCO) of 100 kDa had

lower permeate flux than a PVDF membrane with a 50 kDa MWCO. This could be due to different fouling mechanisms (i.e., pore blockage and cake formation). The pore blockage was attributed to the presence of large pores in the PVDF membrane with a 100 kDa MWCO. Large pores are easily available for particles, resulting in particles blocking the pore mouth by bridging or blocking the pores as a result of depth filtration. For the PVDF membrane with a 50 kDa MWCO, separation initially occurs by screen filtration as particles and macrosolutes are unable to penetrate the membrane pores. This leads to fouling by cake formation (47).

Summary of Manure Pretreatment Methods
The choice of pretreatment method depends mainly on the planned strategy for ammonia recovery. In general, most of the membrane processes available for ammonia recovery will require polishing via MF, UF, or a combination of chemically induced flocculation with flotation and filtration. This increases operational costs. On the other hand, most of the physicochemical methods have lower demands on particles removal. These requirements can usually be fulfilled by solid-liquid separation or chemically induced flocculation combined with filtration.

TECHNOLOGIES FOR AMMONIA RECOVERY

Membrane Processes
Nanofiltration
Nanofiltration membranes are characterized by a MWCO in the range of 150–300 Da, which typically displays a very high rejection (> 99%) of multivalent ions, high rejection of organic molecules larger than the MWCO (> 90%) and lower rejection of monovalent ions (48). The latter can be between 0% and 70% (48). Therefore, NF should not be efficient in the recovery of ammonia as isolated molecule or ion. An example is X-FLOWs NF50 M10 membranes with reported retentions of NaCl and $MgSO_4$ of 35% and 94%, respectively.49
It is to be expected that the rejection patterns of ammonium ion (NH_4^+) in the hydrated form is comparable to the potassium ion (K^+) (50).
Total ammoniacal nitrogen present in manure is divided between ammonia (NH_3), which permeate freely through dense NF membranes, and ammonium (NH_4^+) ions, which are actually retained by membranes due to loose complex formation with anions in the manure such as HCO_3^-, PO_4^{3-}, and VFAs (51). This effect has been seen as well in RO membranes (will be discussed in the Reverse Osmosis section). Adjustment of manure pH can be useful in combination with NF depending on whether retention or permeation of TAN is the aim: low pH favors ammonium (NH_4^+) retained with complexes, where high pH favors free ammonia with higher permeation. Therefore, nanofiltration can concentrate or separate soluble nutrients from pig slurry and be used for water recovery. Konieczny et al. (44) used an integrated system of centrifugation/two-step ultrafiltration/nanofiltration to obtain a filtrate with an ammonium (NH_4^+) concentration of 96–135 mg·l^{-1} and total organic carbon (TOC) with 7.6–10 mg·l^{-1}. This filtrate could be used as sanitary safe water applicable for flushing animals, farmhouses or for irrigation purposes (44). Kertesz et al. (52) used a classical cross-flow process and a vibratory shear-enhanced process (VSEP) to reduce total volume and dry matter of the liquid fraction from centrifuged pig manure. The VSEP thin film composite (TFC) polyamide membrane gave higher fluxes and better total soluble solids retention (93.59%) compared to the cross-flow module (58.82%) (52).
The obtained lower fluxes using the cross-flow module are caused by concentration polarization and cake formation. Concentration polarization leads to a concentration gradient of ions or molecules near the membrane surface and thus to a local increase in osmotic

pressure. Organic molecules are likewise accumulated, which promotes gel formation (53). Kertesz et al. (52) reported a rapid flux decrease from 40 to 8.6 l·m^{-2}·h^{-1} in the first few minutes of the cross-flow process. This can be caused by concentration polarization and later by a gel layer formed from the accumulated particles at the membrane surface. Furthermore, Konieczny et al. (44) observed a flux decline after 1.5 h, caused by fouling and scaling.

Fouling is a complex function of physical and chemical properties of feed (pH, ionic strength, concentration, temperature), foulants nature, hydrodynamics conditions, and membrane characteristics (pore geometry, surface charge, surface roughness, and hydrophobicity) (54). By identifying the key parameters responsible for the flux deterioration, it is therefore possible to mitigate fouling.

Initially, the flux decline can be countered by applying higher cross-flow velocities generating high shear forces in the liquid layer at the membrane surface. This reduces the concentration gradient and leads to better flux (45). Intermittent washing with pure water have also been shown to enhance membrane performance (44). Furthermore, using hydrophilic membranes reduce the probability of fouling (53) because hydrophobic membranes are more prone to interact with hydrophobic manure components such as proteins (55). Surface roughness also has an impact on hydrodynamics and additionally offers nucleation sites, hence may induce fouling (56). In addition, tighter membranes are generally less prone to fouling due to reduced probability of pore blocking (57) as previously mentioned.

The pretreatment with chemicals and filtration as described by Hoeksma et al. (31) should also work for NF, but we have found no experimental evidence of this.

To conclude, a combination of pretreatment consisting of centrifugation, followed by UF to remove suspended solids combined with appropriately selected equipment to improve NF performance ensures an effective NF operation with reduced fouling.

Reverse Osmosis

RO just as nanofiltration allows concentration of ammonium. At the same time, RO produces water applicable for flushing animal houses (58). If the RO permeate is subjected to consecutive RO cycles or is treated with zeolites (59) or ion exchange resins (32,34), the permeate can be discharged as clean water directly to the environment. Reverse osmosis can also reduce the volume of animal wastes. In a case of pig slurry, the reduction was 60%, while for hog sow slurry the reduction was 77% (37,60). A summary of recent studies on RO is presented in Table 3.

Table 3 Summary of experimental RO treatment of manure

Reference	Feed	Membrane	Operating condition	Cleaning methods	Permeate quality	Problems
Bilstad et al. (68)	Lab scale: digested swine manure TS 22-32 g l^{-1}, COD 22-25 g l^{-1}, TN 3.4 g l^{-1}, pretreatment: Screw press and polymer addition Full scale: raw manure TS 35-50 g l^{-1}, COD 40-450 g l^{-1}, TN 3.5 g l^{-1}	Lab scale: 18 tubular Polyamide (**PA**) membranes,12.5 mm diameter, length 1219mm, area 0.861 m^2 Full scale: 18x2.6m^2 tubular Polyamide (**PA**) membranes,12.5 mm diameter, length 3660mm, area 46.8 m^2	Lab scale: pressure < 70 bar, temperature < 70°C, 3 <pH<11 Full scale: pressure 40 bar, flux 5-20 L m^{-2} h^{-1}	0.3 % HNO3 at 40°C for 45 min, alkaline detergent (Ultrasil 11) at 40°C for 45	TS 0.22-1.6 g l^{-1}, COD 0.22-1.25 g l^{-1}, TN 0.03-0.34 g l^{-1}	Fouling
Pieters et al. (37)	Sow slurry: TS 15-20 g l^{-1}, pretreatment:	Polysulfone support (**PSU**) with a thin	Pressure 30 bar, mean flux 33.3 L m^{-2} h^{-1},	NA	Total removal of TS, NH$_4$-N	NR

					0.1÷0.2 g l^{-1}	
	sedimentation and bag filter 100 μm and microfiltrated with ceramic membrane	Polyamide (**PA**) top layer, spiral wound Filmtec membranes type BW30-4040 with area 6.5 m^2	concentration factor 1.3, temp. influent 20.6°C, temp. filtrate 21.3°C			
Thörneby et al. (60)	Pig manure TS 22 g l^{-1}, NH$_4$-N 2.8 g l^{-1}, pretreatment: screw press and prefiltered with 100 μm screen.	Tubular membrane AFC99 (PCI Membrane Systems UK), Polyamide (**PA**) area 0.9 m^2	Pressure 30 bar, Temperature 25°C, mean flux 20-25 L m^{-2} h^{-1}	Chemical cleaning with 1%wt alkaline detergent (Ultrasil 10 from Henkel) at 50°C for 45min	Permeate: TS 0.22 g l^{-1}, TN 0.11-0.27 g l^{-1}, NH$_4$-N 0.08-0.2gl^{-1}, Retentate: NH$_4$-N 8.1 g l^{-1}.	Fouling
Fleming and Alpine al. (58)	Raw swine manure & digested swine manure: TS 13-31 g l^{-1}, NH$_4$-N 2.0-2.2 g l^{-1}, P 0.3-0.8 g l^{-1}, K 2.1-2.6 g l^{-1}, pretreatment: pre-filtered 3 times through a 150 μm screen	VSEP-RO (New Polyamide (**PA**) Logic, Emeryville, California), stack of 18 membranes with total area 1.55 m^2	Flux for digested manure 30.5 L m^{-2} h^{-1}, for untreated 23.6 L m^{-2} h^{-1}	NA	NH$_4$-N 13 g l^{-1}, Total P,K removal TS 2 g l^{-1},	Fouling
Masse et al. (51)	Swine manure: TS 1.1 g l^{-1}, NH$_4$-N 0.6 g l^{-1}, pretreatment: Vacuum filtration through diatomaceous earth	Polyamide (**PA**) with area 23.2 or 46.4 cm^2	Pressure 27.6 bar, temp. 21±2°C	Washing with water &, alkaline cleaning NaOH pH 10.5, 1h, 35°C	Retenteate: NH$_4$-N 10 g l^{-1}, Permeate NH$_4$-N 0.02 g l^{-1},	NR
Mondor et al. (70)	Swine manure: TS 10-16 g l^{-1}, pretreatment: vacuum filtration concentrated by electrodialysis	Polyamide (**PA**) TFC-HF (Koch, Wilmington, MA, USA), diameter 39mm	Pressure 55 bar, temp. 21÷24°C	NI	Permeate: TS 1.2 g l^{-1}, NH$_4$-N 0.6 g l^{-1}, Concentrat: TS 40.5 g l^{-1}, NH$_4$-N 12.8 g l^{-1}	NI
Kertesz et al. (52)	Pig manure, pretreatment: Centrifuged	VSEP-RO: Thin film composite Polyamide (**PA**) (Hydranautics) Cross flow: GE Osmonics	Pressure 35 bar, Temperature 25 ±2°C max. flux 71.06 L m^{-2} h^{-1} for VSEP-RO and 28.6 L m^{-2} h^{-1} for cross flow-RO	After each run washed with deionized water	TSS removal VSEP-RO 95.14%, cross flow-RO 87.94%	NR
Masse et al. (62)	Swine manure, TS 16.5 g l^{-1}, pretreatment: with vacuum filtration & perforated belt conveyor	Lab-scale: Polyamide (**PA**), area 11.6 cm^2 Pilot-scale: spiral wound area 7.4 m^2	Lab-scale pressure 41-83 bar, temperature 21±2 °C, max, flux 27 L m^{-2} h^{-1} Pilot-scale pressure 48 bar, temperature 21.1±1.1°C, max, flux 36 L m^{-2} h^{-1}	Washing with water for 16h, alkaline cleaning (pH 10, 37°C) for 1 h	The concentrate: NH$_4$-N 6.4-6.7 g g l^{-1}, permeate NH$_4$-N 0.2 g l^{-1}	Fouling

Vaneeckha ute et al. (81)	Animal manure, maize and food residue: TS 82±17 g l^{-1}, pretreatment: Polymer and rotating drum filtration	NI	NI	Citric acid	VSEP1: N 0.13 g l^{-1}, COD 473± 67 mg l^{-1}, VSEP1: N 0.09±0.04 g l^{-1}, COD 92±42mg l^{-1}	NI
Masse et al. (144)	Swine manure, TS 19.4-27.3 g l^{-1}, SS 19.4-27.3 g l^{-1}, NH$_4$-N5.9-6.4 g l^{-1}, pretreatment: perforated belt conveyor, decanted bag filtration 800 µm, UF 25 kDa	Spiral wound BW 30 (Dow), area 7.2 m^2	Pressure 41 bar, temperature 20.3±0.6 °C, flux 10.4-11.3 Lm^{-2} h^{-1}	Washing with EDTA 2mM and STPP 2.7 mM for 1 h, alkaline cleaning (pH 10.9, 40°C) for 1 h, soaking in permeate for 72 h, cross flow 11.5 cm s^{-1}	NH$_4$-N 0.1-0.2 g l^{-1}	Fouling problem when SS is above 4 g l^{-1}
Ledda et al. (59)	Digested swine manure, TS 9.5±0.5 g l^{-1}, SS 1.1±0.4 g l^{-1}, NH$_4$-N 1.8±0.02 g l^{-1}, pretreatment: polymer and screw press, UF 40 kDa	2 consecutive RO (Dow)	NI	NI	Permeate: TS 0.34±0.04 g l^{-1}, NH$_4$-N 72.2±9.1 mg l^{-1} Retentate: TS 32±2 g l^{-1}, NH$_4$-N 7.3±0.07 g l^{-1}	NI
Masse et al. (145)	Swine waste water, TS 14.4±0.4 g l^{-1}, SS 3.5±0.4 g l^{-1}, NH$_4$-N 3.6±0.1 g l^{-1}, pretreatment: perforated belt conveyor, decanted bag filtration 800 µm, cartridge 10 µm	Spiral wound BW 30 (Dow), area 7.2 m^2, Spiral wound SW 30 (Dow), area 7.4 m^2	Cross flow 4.4 cm s^{-1} BW 30: Pressure 40.7 bar, temperature 20.5±0.5 °C, flux 6.4 L m^{-2} h^{-1} SW 30: Pressure 52.5 bar, temperature 20.3±0.6 °C, flux 10 Lm^{-2} h^{-1}	Washing with EDTA 2mM and STPP 2.7 mM for 1 h, alkaline cleaning (pH 10.9, 40°C) for 1 h, soaking in permeate for 72 h, cross flow 11.5 cm s^{-1}	BW 30 retentate: TS 26.4-27 g l^{-1}, SS 5.9-6.5 g l^{-1}, NH$_4$-N 6.2-6.3 g l^{-1} SW 30 retentate: TS 26.9±0.8 g l^{-1}, SS 6.1±0.2g l^{-1}, NH$_4$-N 6.6±0.1 g l^{-1}	Membrane compaction
Masse et al. (33)	Swine manure, TS 10.4±1.9 g l^{-1}, SS 1.1±0.4 g l^{-1}, NH$_4$-N 2.6±0.6 g l^{-1}, pretreatment: High molecular weight polymer, rotary filter, NF	Spiral wound NF (PVDF, Hydranautics), area 7.0 m^2, RO: LFC3 (PA, DOW), area 7.4 m^2, SWHR-LE (Dow), area 7.0 m^2	Cross flow 4.4 cm s^{-1} Temperature 21-23 °C NF: Pressure 17 bar, LFC3: Pressure 38 bar, SWHR-LE: Pressure 59 bar	NF and LFC3: Washing with alkaline NaOH and hypochlorite (pH 9, 38°C) for 1 h, soaking in permeate, acidic cleaning SWHR-LE: acidic cleaning	NF retentate: TS 6.7-13.3 g l^{-1}, SS 0.8-1.3 g l^{-1}, LFC3: retentate: TS 9.5-12.7 g l^{-1}, SS 1.0-1.7 g l^{-1}, SWHR-LE: retentate: TS 9.6-9.8 g l^{-1}, SS 0.7-1.0 g l^{-1},	Fouling problem at low SS

NI - no information

Polyamide (PA) membranes have frequently been used for manure treatment with RO (Table 3). This is due to their high selectivity toward salts and broad pH operating range (39,61). Improved performance can be achieved when the slurry is first microfiltrated or vacuum filtrated (37,62). Properly chosen pretreatment based on Silt Density Index (SDI) for the selected membranes is a key for long-term RO system operation. This is despite the fact that there is no linear correlation between the SDI index and the concentration of foulants (63,64). More pretreatment is required for untreated manure compared to digested manure as undigested manure contains larger particles.58 VSEP systems require removal of larger particles, where 100 or 150 μm prescreens have been used for both digested and undigested pig slurry and hog manure on farms in Korea, Japan, the United States, and Canada (58,60,65–67). The pretreatment process described by Hoeksma et al. (31) and Foged (32) makes it possible to use spiral wound cross-flow RO systems. At least five manure separation plants are currently running in the Netherlands based on this principle (31,32).

Compared to nanofiltration, obtained fluxes are lower even when higher pressure is applied (Table 3), although Kertesz et al. (52) has reported permeate fluxes almost identical to NF fluxes when a VSEP system was used (68 and 71 $l \cdot m^{-2} \cdot h^{-1}$, respectively). For sow slurry, higher fluxes were also obtained by increasing concentration factors from 1.3 to 4.1 and by subjecting the permeate to a second microfiltration step (37). VSEP systems succeeded in removing 95% of total soluble solids, while traditional cross-flow mode only removed 88% (52). Based on Hoeksma et al.'s data (31) slurry from fatteners and sows pretreated by flocculation, aeration, and filtration treated by a crossflow RO succeeds with the removal of solids above 98%. This is close to the results obtained by Johnson et al. (67) who reported 100% removal of TSS for cow manure. For a VSEP RO system, digested manure showed larger fluxes (30.5 $l \cdot m^{-2} \cdot h^{-1}$) and water recovery (75%) than for untreated pig slurry (23.6 $l \cdot m{-2} \cdot h{-1}$ and 50%, respectively) (58). The permeate quality is also slightly better for an anaerobically treated manure compared to raw manure.68 Better results have been presented by the manufacturer of VSEP, New Logic (65). The reported water recovery from hog manure was 80% (65). TAN retention was in the range of 93% to 99.8% producing concentrate with TAN between 6–10 $g \cdot l^{-1}$.51,62 This is similarly to what Hoeksma et al. (31) and Hoeksma and de Buisonjé (69) reported for four spiral wound cross-flow RO full-scale plants. They found TAN retentions above 95% with concentrations between 4 and 8 $g \cdot l^{-1}$. Even better results were obtained when swine manure was subjected to electrodialysis prior to RO producing concentrate with 13 $g \cdot l^{-1}$ of NH_3-N (70).

A rapid decrease of flux was observed during separation of pig slurry indicating concentration polarization and fast deposition of particles on membrane surfaces (60). Massé et al. (62) reported a flux decrease from 27 to 18 $l \cdot m^{-2} \cdot h^{-1}$ in laboratory scale experiments and a flux decrease from 36 to 8 $l \cdot m^{-2} \cdot h^{-1}$ in pilot scale runs due to concentration polarization. This is in accordance with the results reported by Hoeksma and de Buisonjé (69) from four Dutch manure separations plants. Here, the water flux can be inferred to vary between 4 and 8 $l \cdot m^{-2} \cdot h^{-1}$.

Performance of RO is a function of feed temperature and total solid content (60,65). A warmer feed is less viscous and more soluble in the membrane. This leads to a higher permeability in the membrane. Similarly, a lower total solid content increases the flux by reducing fouling, concentration polarization and osmotic pressure.65 In the case of pig manure, an increase of temperature from 10 to 20°C raised the flux 50% with a subsequent loss of ammonia (60,68). Higher fluxes reduce the size of RO plants, thus reducing the investment costs. Pressure increase for reverse osmosis from 30 to 60 bar decreased COD, NH_3-N, total N and K concentrations in the permeate (37). However, when the pressure was increased above 20 bar, concentration polarization increases at the membrane surface, which

resulted in an increase of osmotic pressure (62). Therefore, to be able to use RO technology, it is necessary to use membranes that can sustain high applied pressure (62).

Lowering the pH from 8.2 to 6.2 prevents deposition of poorly soluble salts on the membranes. It also has a positive effect on removal of P and N, but a negative effect on COD as it may decrease rejection of molecules responsible for COD in the permeate (e.g., unionized volatile fatty acids [VFAs], which can pass the membrane) (37,51). As described previously, lowering pH or temperature shift the equilibrium toward NH_4^+. Thus NH_4^+ has higher retention, due to complexes formation (37,51). In the case of raw sow slurry, TAN retention increased from 82% to 92%, when pH decreased from 8.2 to 6.2. For digested manure, when pH dropped from 8 to 4, retention was nearly 100% (37,68). Massé et al. (51) reported 99% retention of NH_4^+ at pH below 6.5 when concentrated sulfuric acid was used for manure acidification. Acidification of the manure though has no influence on the flux, but can successfully convert carbonates to carbon dioxide. This minimizes the risk of scaling (63,68). Moreover, the surface charge change with pH for some membrane materials like for instance PA, so PA develops a positive surface charge when operating below the isoelectric point of the membrane (pH 4–5 for PA). This can also enhance NH_4^+ retention as pH does not only change the feed properties (51,71).

Fouling has also been a problem during RO operation. Even when VSEP systems have been used, fouling appeared. This happens especially during filtration of digested manure containing mainly smaller particles (58). However, if colloidal or suspended solids have been removed, compared to porous MF or UF membranes, the risk of surface fouling is reduced (72). Furthermore, chemical cleaning with a 1%wt alkaline detergent restores the original flux (51,60,62,68).

Electrodialysis

Electrodialysis enabled production of a concentrate with 14 g·l^{-1} NH$_3$-N (70). Mondor et al. (70) concluded that thin and more conductive cation/anion exchange membranes: CMX/AMX and CMB/AMX-SB membranes had a higher NH_4^+ transfer rate than cation exchange membranes LMP/AR 103 QDP due to a higher current for a given voltage applied. It was found that around 75% of the current was used to transfer the ammonium, whereas the rest was lost as heat or used to transfer other cations such as potassium. Unfortunately, after 2 h of manure filtration, AMX-SB membranes cracked and also on CMX membranes spots were observed suggesting fouling. Cleaning procedure composed of chemical cleaning with 0.5% NaOH for 20 min, rinsing with water, cleaning with 1% HCl for 20 min, and again rinsing with water was used. It resulted in complete restoration of the CMB membrane and almost complete restoration of AMX membranes (91%) (73). Analysis of the foulants revealed presence of oxygen, calcium, and silica (73). Moreover, a dark color on the AMX membrane indicates that fouling possibly is organic in nature (73). Removal of ammonium and other cations therefore seems possible using ED, but further investigations are needed.
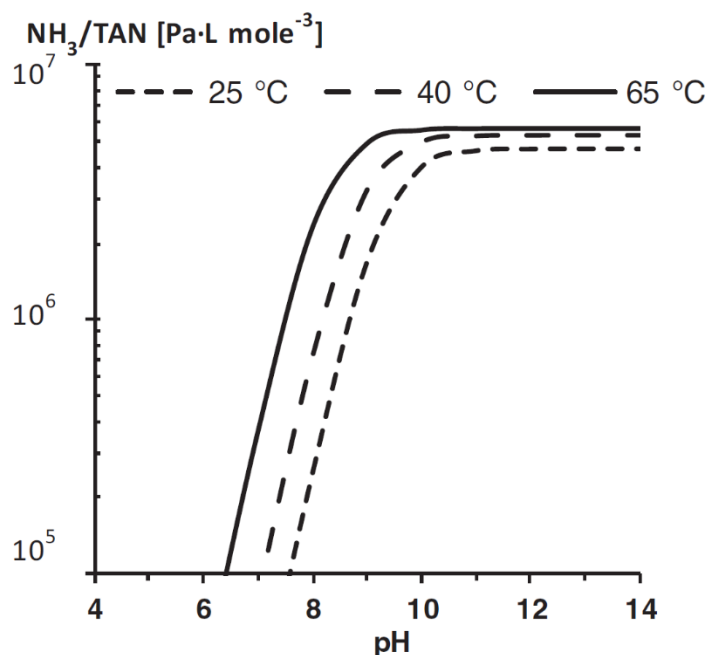
Figure 1 Influence of temperature and pH on the ratio of ammonia partial pressure to total ammoniacal nitrogen (TAN) concentration ($- 65 \circ C, - 40 \circ C, \cdots 25 \degree C$).

Membrane contactors

As alternative to separating ammonia from the slurry using RO the difference in vapor pressure between the slurry constituents can be used. This approach is used in conventional ammonia stripping using packed columns (air stripping) and in membrane contactors (MD). In order for the total ammoniacal nitrogen (TAN) to evaporate it has to be in the form of ammonia. The equilibrium that governs this reaction is

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \tag{1}$$
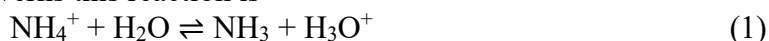
The equilibrium and hence solubility of ammonia in slurry is influenced by temperature and to a lesser extent by the ionic strength of the slurry.

As seen from figure 1, ammonia vapor pressure ratio to the total TAN is more influenced by pH than by temperature. As the water vapor pressure also increases with temperature a high pH, but a moderate temperature is to be preferred in order to get high ammonia removal but low water removal.

In MD, the alkalinized slurry is brought into contact with a porous, hydrophobic membrane. The nonwetted membrane will reject liquid but will allow vapor to pass through the pores. On the permeate side in MD, an acid solution is used to absorb the NH_3 vapor, the typical acid being sulfuric acid (H_2SO_4) leading to ammonium sulfate (NH_4)$_2SO_4$ formation. As the vapor pressure of (NH_4)$_2SO_4$ is zero in acidic solutions, the driving force for the process is the alkaline NH_3 vapor pressure alone.

Membrane distillation successfully removed ammonia from digested manure in lab and pilot scale and from wastewater in industrial scale (74,75). When pH in the slurry was raised above 9 by alkali addition, a NH_4^+-N concentration of 53 g·l^{-1} could be reached in the permeate (76). Du Preez et al. (23) used a polypropylene (PP) membrane using several pretreatments such as ultrafiltration and chemical precipitation for anaerobically digested pig manure achieving ammonia removal efficiencies between 99.2–99.9%. Without any pretreatment, Waeger-Baumann and Fuchs (77) used a PP membrane at pH 10 and a temperature of 40°C obtaining 98.5% ammonia removal. The N-depleted manure produced had a concentration of 42 mg NH_4^+-N per l.

As in reverse osmosis, increasing temperature and pH enhanced ammonia mass transfer. By increasing the temperature from 15 to 70°C, ammonia mass transfer increased almost 10 times (23). Even at a pH above 10, an increase in temperature has a pronounced effect on ammonia removal efficiency (23). This is mainly caused by an increase in the diffusivity of ammonia in the gas and liquid phase and a decrease in slurry viscosity, both effects leading to a higher mass transfer rate. The membrane distillation module configuration also has an impact on the mass transfer rate and thus economy of the whole process (77). When manure is introduced to a tubular membrane on the lumen side, it requires prior removal of suspended solids (e.g., by ultrafiltration to avoid clogging the membrane module), while when manure is introduced to the membrane on the shell side the pretreatment step can be omitted (23,76,77). However, one of the disadvantages using this configuration might be a nonuniform flow as a result of channel formation, bypassing, mixing, and dead zones which decrease mass transfer efficiency (78). When ultrafiltered slurry permeate was introduced on the lumen side, the transfer rate was about 1.5 times higher compared to when the feed was introduced on the shell side (77). The results obtained for untreated manure digestate fed to the shell side of the module were slightly lower than results for ultrafiltered permeate (77). This is in agreement with Ahn et al. (79), who reported inhibitory effects of suspended solids on mass transfer while using polytetrafluoroethylene (PTFE) membranes. However, it should be investigated further if a higher mass transfer rate is more economically advantageous when manure is introduced on the lumen side, than when manure is introduced on the shell side, because no solid removal step is required in the latter case.

Table 4 Comparison of membrane modules for ammonia removal

	Module				
Characteristic	Plate and frame	Spiral-wound	Tubular	Hollow fiber	Capillary
Resistance to fouling (39)	Good	Moderate	Very good	Poor	Poor
Ease of cleaning (39)	Good	Fair	Very good	Poor	Poor
Relative cost (39)	High	Low	High	Low	Low
Application (39)	UF, NF, RO, ED, MD	RO	MF, UF, RO, ED, MD	MF, MD	MF

Comparison of membrane processes

In 2007, Massé et al (80) reviewed most of the membrane technologies for manure treatment. The review identified reverse osmosis as the most efficient for nutrient concentration, though limited at industrial scale by high cost of operation. In this review, membrane technologies are compared based on module type (Table 4), processes (Table 5), and materials (Table 6). Table 4 presents membrane technologies for ammonia recovery categorized according to the applied module. Five main categories can be distinguished: plate and frame, spiral wound, tubular, hollow fiber, and capillary.

In most cases, flat sheet or tubular membranes have been used for manure processing because they are easier to clean (39). Hollow fiber and capillary membranes are more prone to fouling or pore blocking by particulate matter. Hence, they are difficult to clean and therefore require more feed pretreatment, except when they are used in membrane distillation configuration with the manure fed to the shell side (39,76,77).

Karakashev et al.(36) reported difficulties with cleaning submerged capillary membranes with air and water, as membranes clogged totally after 3–4 days of operation. Nearly all researchers using UF have applied tubular membranes, except Konieczny et al. (44), who

applied flat sheet membranes. Flat sheet membranes with low cutoff were reported as easy to clean using only deionized water, because only cake formation has happened. For NF and RO, the flux can be restored using chemical cleaning for both flat sheet and tubular membranes (51,52). In some VSEP systems, only water is needed (52), while in others the use of a special blend of surfactants and chelating agents such as NLR 505 and NLR 40467 or citric acid (81) is recommended. Spiral wound membranes have been used by Massé et al. (62) and Pieters et al. (37) and are used in full-scale plants in the Netherlands (31). Massé et al. (62) cleaned the membranes with water for 16 h restoring 94% of the original flux and with an alkaline solution for 1 h to reach the original flux. In the case of Pieter et al. (37), the latter membrane cleaning was not required because the manure had been microfiltered before and suspended solids thus removed. As presented in Table 5, synthetic membranes for ammonia recovery can be divided into two groups based on their structure (morphology): dense and porous membranes. Dense and porous membranes are distinct from each other based on the size of the separated particles and molecules. Dense membranes are usually composed of a thin layer of a dense material rejecting suspended macromolecules, multivalent ions, and monovalent ions (NF, RO), while a porous membrane retains only suspended solids and bacteria (MF, UF) and viruses and macromolecules in the case of UF. The porous membranes take use of screen or depth filtration, where fouling in screen filtration is present on the membrane surface and is more accessible for water and cleaning agents.

Table 5 Comparison of membrane processes for ammonia removal

Technology	Separation principle	Size range	Morphology	MWCO
Microfiltration	Size	0.1-0.5 µm	Porous membrane	Poor
Ultrafiltration	Size	0.01-0.04 µm	Porous membrane	5-100 kDa
Nanofiltration	Size, charge	NI	Dense membrane	0.2 kDa
Reverse osmosis	Affinity	NI	Dense membrane	NI
Membrane distillation	Vapor pressure	NI	Porous membrane	NI
Electrodialysis	Charge	NI	Ionic membrane	NI

NI = not enough information available.

Table 6 Comparison of membrane materials for ammonia removal

	Polymer								Ceramic	
Properties	PA/PSU	PA	PP	PTFE	PVDF	PSU	PES	MCE	Al_2O_3	TiO_2
ϒ mJ m^{-2}	20-30 (146)	46.2 (83)	30.5 (83)	19 (147)	40.2 (148)	41 (147)	32.09 (149)	45 (150)	67 (151)	61.5 (152)
Θ °	61.42 (146)	72.7 (83)	108.6 (83)	98 (153)	90 (153)	75 (154)	95 (155)	89 (156)	36 (151)	44 (152)
W$_{ad}$ mJ m^{-2} *	107.42	94.71	49.6	62.84	73.00	91.89	66.64	74.27	Low	125.51
Thermal stability**	50	52	-20	115	-35	185	190	105	132.06	1668
Process	RO	RO, NF	MD	MD	UF	UF	UF	MF	MF	MF

ϒ surface energy, Θ contact angle, Wad calculated using the Young-Dupree equation, Thermal stability based on Tg (◦C) for the polymers and on the melting point (◦C) , and for the ceramic.

At low pH, NF and RO will retain TAN in ammonium form due to the rejection of the larger counter anions present in manure such as HCO_3^-, PO_4^{3-}, and VFAs. At higher pH, MD will allow TAN in the form of free ammonia to evaporate through the membrane to be captured in an acidic stripping solution.

The selection of an appropriate method for ammonia recovery has to take economics into consideration. The total cost of the installation is the sum of total capital investment (TCI) and operating costs. TCI includes costs of tanks, separation units (membrane/column), pumps (feed/circulation/turbine), compressors, and pretreatment and posttreatment methods [39]. Operating costs contain energy consumption, replacement of equipment, labor costs, and maintenance [39]. Energy requirements can be estimated from flow rates, pressure differences, cross-flow velocities, and surface areas [39].

In pressure driven processes such as MF or UF, two types of pumps are employed: Feed pumps to pressurize the feed and circulation pumps to control cross-flow velocity in order to mitigate concentration polarization and fouling [39]. Energy consumption is governed by the circulation pumps that deliver high cross-flow velocity, rather than by the feed pump, which only has to deliver a relatively low pressure increase for the feed compared to other membrane processes [39]. The energy requirement of a pump (E_p) can be calculated from equation 2, where q_v is the flow rate ($m^3 \cdot s^{-1}$), η pump efficiency (0.5–0.8) and ΔP pressure difference.

$$E_p = \frac{q_v \cdot \Delta P}{\eta} \tag{2}$$

Table 7 Energy demand of ammonia recovery methods

Technology	Refrences		Energy consumption	
		Manure pretreatment	kWh m^{-3}	kWh (kg NH$_3$)$^{-1}$
Ultrafiltration	(43,45)		2.3 – 8.8	
		Ammonia Recovery methods		
Nanofiltration	(52)		2.2	
Reverse osmosis	(60,68)		4.3-5.5	
Membrane distillation	(77)		0.25	0.18
Air stripping			4.1	3.1
Ion Exchange			0.053	0.04
Chemical Precipitation			0.84	0.63

Energy requirement of a turbine (E_t) in NF and RO also depends on the turbine used for energy recovery and is given by equation 3.

$$E_t = -q_v \cdot \Delta P \cdot \eta \tag{3}$$

Assuming 65% pump efficiency, the approximate energy consumption per 1 m3 of feed have been calculated using equations 2 and 3 for the respective membrane technologies based on data from selected literature examples. It can be seen from Table 7 that RO and NF have energy consumptions of the same magnitude, as those processes are very similar. The energy consumption of the total process will be larger as pretreatment steps are necessary prior to NF or RO (Table 8). Fuchs et al. [82] reported the energy consumption of RO with a prior UF step to be in the range 16–25 kWh m^{-3}. As a comparison, the energy consumption per m^3 of slurry treated at the Kumac Mineralen plant is reported to be 9.2 kWh. As 80% of the slurry ends in the liquid phase, this equals 12 kWh per m^3 of feed to the RO unit or between 0.77 and 1.3 kWh per kg NH$_3$ [32]. As the data from Kumac Mineralen includes pretreatment and

post treatment, this tallies well with the estimated energy consumptions and as a rough estimate RO consumes 50% of the energy necessary for the ammonia recovery process. In case of the MD, process energy consumption is at least nine times less compared to other membrane processes. As this is highly dependent on the pressure drop, the energy consumption can be even further reduced by changing the module configuration from capillary to tubular. However, the MD process should not be directly compared with pressure driven membrane processes, because it is more similar to air stripping (AS) based on the working principle. This will be discussed in more detail in the physicochemical methods section.

Total energy consumption in ED is the sum of electrical energy needed to drive the ionic transfer and pump requirements to run the concentrated and depleted streams and the anode/cathode rinse solutions, meaning that the whole process is rather energetically demanding (39) Unfortunately, insufficient data is available in the literature to make an energy requirement calculation possible.

Table 8 Total cost of ammonia recovery methods including necessary pretreatmen and chemical addition

Technology	Energy consumption	Energy cost	Chemical Cost	Operating Cost (Energy & chemicals)
	kWh m^{-3} feed	US$ m^{-3} feed	US$ m^{-3} feed	US$ m^{-3} feed
UF/NF	4.5-11	0.3 - 0.8	0.7[a]	1.0 – 1.5
UF/RO	6.6 – 14.4	0.5 – 1.0	0.7[a]	1.2 – 1.6
MD	0.2	0.02	3.5[c] 1.1[d]	3.52 1.12
UF/MD	2.5 – 9.1	0.2 – 0.6	3.5[c] 1.1[d]	3.7 - 4.1 1.3 – 1.7
AS	4.1	0.3	3.5[c] 1.1[d]	3.8 1.4
CP	0.8	0.1	12.9	13.0
UF/IE	2.3 - 8.9	0.2 – 0.6	8.7	9.3

[a]Consumption and cost of concentrated acid to decrease pH below 4.5 has been taken from Massé et al. (51).
[b]Assuming electricity cost 0.07 US$ (kWh)$^{-1}$ (163).
[c]Consumption and cost of NaOH to increase pH above 10.5 has been taken from Zhang and Jahng (110) and Zhanjiang Chikan Huanan Chemical Industry Co.(164).
[d]Consumption and cost of lime to increase pH above 10.5 has been taken from Liao et al. (109) and Dinh Ha Import Export Co. (165).
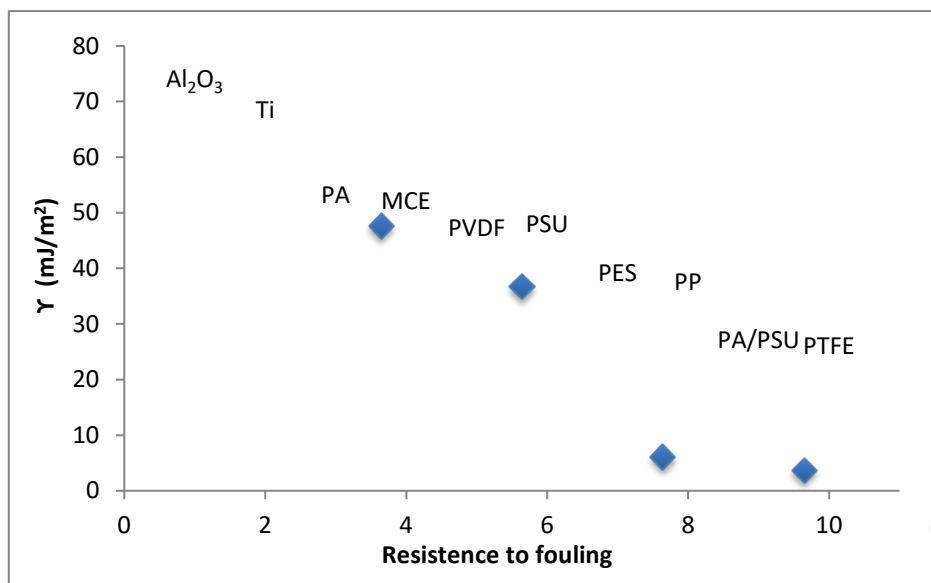
Figure 2 Proneness to fouling with respect to surface energy.

Influence of membrane material on process conditions

Membranes for ammonia recovery can be made from organic or inorganic materials including ceramic and homogeneous organic films (polymers). Ceramic membranes are formed from inorganic materials such as aluminum oxides and sintered titanium. Those membranes are very resistant to aggressive media such as acids and organic solvents. They are also very chemically, thermally, and mechanically stable, and biologically inert. The high weight and substantial production costs of ceramic membranes compared to polymeric membranes for some applications are balanced by their long expected lifetime (83). To our knowledge, currently, ceramic materials are only produced in the tight UF range with MWCO down to ~450 Da (i.e., Inopor) and additional at much higher prices than polymeric membranes. Thus, polymeric materials are the only choice for the time being. Research is ongoing to make ceramic membranes for NF and RO, but as yet a commercial breakthrough is waiting (84,85). At present, the polymeric membranes lead the ammonia recovery industry market due to both performance and price.

Commercial polymers —polysulfone (PSU), PA/PSU, PA, PES, MCE, PP, PTFE, and PVDF—are used industrially for ammonia removal in different process technologies. Nonetheless, the choice of membrane polymer is not a trivial task. As shown in Table 6, the polymer must have appropriate characteristics for the particular application. In the case of MF, UF, NF, and RO process technologies, the polymer has to be as hydrophilic as possible (PA, PSU, PES, MCE) to reduce fouling (39). However, in the case of MD, the microporous membrane should not allow the aqueous solution to pass through the membrane pores, hence membranes have to be hydrophobic (PP, PTFE, PA/PSU, and PVDF) (78). Furthermore, all polymers have to withstand the harsh cleaning conditions and be chemical resistant for solvents and show thermal stability as well.
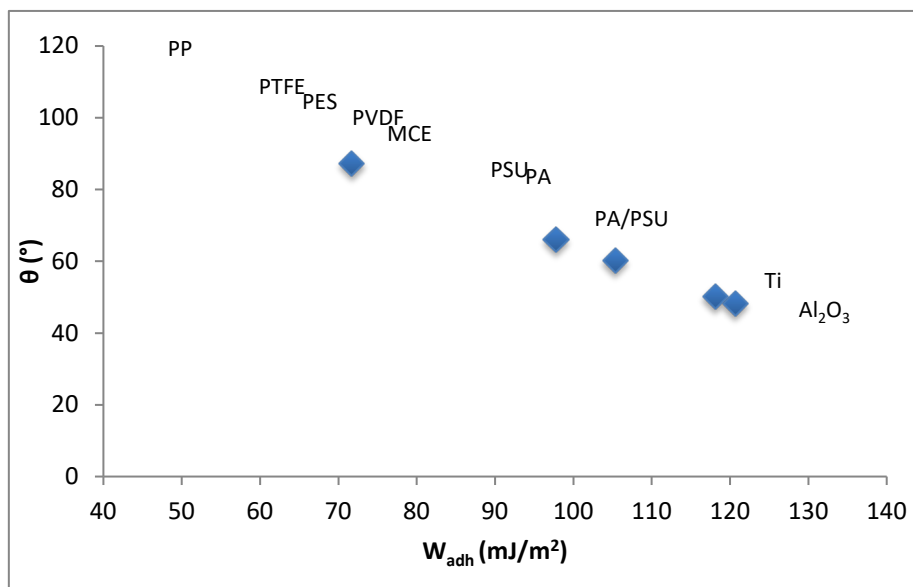
Figure 3 Work adhesions as a function of contact angle.

Surface chemistry strongly influences the properties of a membrane such as chemical or thermal resistance. The hydrophilicity or hydrophobicity of a membrane can be related to surface free energy, while the presence of ionic charge, and binding affinity for particles in a solution can be expressed as the work adhesion value as shown in Table 6. The hydrophilicity and hydrophobicity of membrane surfaces can also be expressed in terms of water (liquid) contact angle (θ). Hydrophilic (water wetting) membrane surfaces have a contact angle θ in the range of 0–90° (closer to 0°), where hydrophobic (not water wetting) materials have θ in the range of 90–180° (83). Kabsch-Korbutowicz et al. (86) demonstrated that the membrane surface free energy and related hydrophilicity/hydrophobicity also influence membrane particle adsorption or fouling phenomena. These conclusions were further supported by the thorough work of Tu et al. (87) Accordingly, Figure 2 shows the relation of surface energy and fouling tendency in ammonia recovery with respect to the surface energy.

High-energy surfaces are more hydrophilic and contain polar and/or ionizable groups. Low energy surfaces are more hydrophobic and are usually polymers of olefins, fluorocarbons, or minimally substituted aromatics. Although the surface energy provides information about the hydrophobic/hydrophilic character of the membranes, it is not enough to understand the wettability of the surfaces. In order to have more accurate characterization of membranes wettability, the contact angles between the liquid (water) and the membranes were evaluated (Figure 3). It can be seen from Figure 3 that PP membranes have the highest hydrophobicity, while Al_2O_3 membranes the lowest.

Table 6 includes also the values of the proneness to fouling determined by the surface energy of the materials. However the process technology has to be considered as well as the fouling resistance. In case of MF, UF, NF, and RO, hydrophilic membranes suffer less from fouling. In MD, the more hydrophobic the surface the less the risk of wetting, but the more it adsorbs organic particles (88,89).

Ceramic membranes used in microfiltration show excellent resistance to fouling (37,90). Likewise, PVDF and PSU membranes performed well in UF (42,44,46). On the other hand, as seen in Table 3 for RO, PA membranes do not show a consistent picture for proneness to fouling. This could be due to varying and insufficient pretreatment methods and difference in degree of hydrophilicity of the PA membranes, as PA exist in different forms (83). Even the most hydrophilic membranes will without proper pretreatment adsorb foulants during long-

term operation. Higher fouling tendency has also been observed for PES membranes (45,46). For MD, PTFE seems to be even less fouling resistant, though it has only been tested in short-term operations by Waeger-Baumann and Fuchs (77).

The ease of cleaning is also associated with the filtration process and the surface chemistry of the membrane. Table 6 shows the ease of cleaning based on the work adhesion values between water and the membrane polymer.

Figure 3 shows the adhesion forces between the water and the membrane surface. There is a larger affinity between water and hydrophilic materials leading to stronger adhesion forces being present at the membrane surface. Similarly, less affinity between water and the hydrophobic surface leads to a lower work adhesion value. This explains the relative ease with which PVDF or PSU membranes can be cleaned with deionized water compared to PES, where chemical agents have to be applied (42,44,45). Also, PA membranes used in RO have been easy to clean, especially when combined with a VSEP system (52).

Summery on membrane processes

It can be concluded that flocculation combined with flotation and filtration or MF and UF are successful methods for removing suspended solids and producing a clear permeate that can be used for further ammonia retention by NF, RO, or MD. The process performance will be greatly influenced by and is highly dependent on presence, composition and potential variations in particles, SS and organic material. This emphasizes that NF and RO performance depends highly on pretreatment and cleaning methods. From the module comparison, it was found that flat sheet and tubular membranes are the easiest to clean. Furthermore, ceramic membranes are the most fouling resistant, and to a lesser extent PA, MCE, PVDF, and PSU membranes. Correspondingly, ceramic membranes are the easiest to clean followed by PA, PSU, MCE, and PVDF. Anaerobic digestion of animal wastes reduces manure solids content and particles size, thus the number of necessary pretreatment steps to membrane processes are also reduced (91). Furthermore, Flemming and MacAlpine (58) and Bilstad et al. (68), reported improved permeate quality, higher fluxes, and water recovery while using digested manure compared to raw manure. Without pretreatment, flux through a MF membrane could decrease by 90%, while with prefilters the flux remained unchanged for nearly 50 days (38). Inappropriate cleaning with aeration could result in foaming, probably due to the presence of bacteria which excrete extracellular polymers (ECP). ECPs act as surfactants decreasing surface tension and result in foaming (92–95). However, in a case of piggery wastewater, more than 10 s of aeration per 10 min permeation successfully decreased the activity of acid-forming bacteria.38 It is reported that cleaning MF membranes with water failed, probably because the foulants were trapped inside the membrane, while frequent water cleaning of some UF and of some VSEP NF membranes could restore original fluxes in case of cake layer formation. Alkaline cleaning could remove biofouling, while acids or an EDTA solution could remove inorganic fouling. Consecutive cleaning with different cleaning solutions should be applied in order to remove both types of fouling, as shown by Lee et al. (38). However, Zhang et al. (45) reported that chemical cleaning with HNO3 and EDTA succeeded only in eliminating inorganic compounds. The best MF permeate quality is achieved using cellulose ester membranes, but the highest flux is obtained using ceramic membranes. In case of UF, the best permeate quality have been achieved using PVDF membranes. PVDF membranes also have lower fouling tendency and are easier to clean than PES membranes. It is also noticed that the cut off value of the membranes is of high importance, as it has been reported by Konieczny et al. (44) that larger pores in membranes are vulnerable to small particles clogging the membrane pores. This will again affect the cleaning efficiency. VSEP in NF has advantages over cross-flow NF with higher fluxes, less fouling, and better TSS retention. Fouling occurs to a lesser extent in VSEP because particles are not so attached to

membrane surfaces and vibrations decrease the concentration polarization and gel layer formation (52). RO can produce concentrate with TAN 10 g·l⁻¹ and permeate down to 0.02 g·l⁻¹ TAN. The permeate can thus be used as sanitary water or if further purified by IE be discharged into nature. If colloidal and suspended solids have been eliminated, fouling can be reduced by acidifying the slurry prior to RO as this removes carbonates and additionally increases Ca-salt solubility thereby reducing precipitation. Nevertheless, chemical cleaning with 1 wt% alkaline detergent is obligatory to retain the original flux of RO membranes. Electrodialysis is another promising technology, which can produce a concentrate with 14 g·l⁻¹ ammonia. However, after 2 h of filtration, ion exchanged membranes revealed the presence of cracks suggesting fouling which might hinder long-term operation. Moreover, ED is a rather energy demanding process; hence it raises the power consumption considerably. Membrane distillation, as reported by Vanotti and Szogi (76) can in laboratory scale produce concentrate with up to at least 53 g·l⁻¹ of ammonia without any pretreatment. On a semi-industrial scale, the BioRek concept required anaerobic digestion and ultrafiltration prior to MD, but achieved 99.2–99.9% ammonia removal (23).

Physicochemical Methods
Air stripping (AS)
Ammonia can efficiently be removed from slurry by air or steam stripping, as reported by Zeng et al. (96) The method involves the use of stripping towers, compressors, and pumps, which introduce air or steam into the liquid phase. When air stripping is used absorption or adsorption towers are needed to recover ammonia from the gas phase. For steam stripping, condensation, or absorption equipment is needed to recover ammonia, though no further post treatment of exhaust gases is required (96). Just as in membrane distillation, the amount of ammonia that can be recovered depends upon two equilibria: gas/liquid equilibrium and ammonia dissociation equilibrium in the liquid (97).

Air stripping or aeration of wastewater has been reported since the beginning of the 20th century (98), mainly for the purpose of removing noxious compounds from the water. It was not until the 70'es that ammonia stripping from wastewater was seriously promoted (99–101). Large-scale installations were implemented at least 9–10 different places in the United States mainly for the purpose of removing ammonia from reject water following dewatering of digested sludge. The ammonia stripped from the water was simply vented to the ambient air. This practice was later abandoned due to environmental considerations and the units were supplied with an absorber unit.

Today, ammonia stripping with subsequent absorptions of the stripped ammonia is in use in many countries all over the world. In Germany alone, it is reported that at least 15 full-scale stripper/absorber plants are in operation recovering ammonia from wastewater (102). Combined stripper/absorber plants operate basically by heating the wastewater fed to the plant to around 45°C and adding NaOH or lime (Ca(OH)₂) until a pH of 10.5–11 is reached. When lime is used, it is normally added in a precipitation tank, which will precipitate carbonates and phosphorous salts before the water is fed to the stripper tower. The recommended volumetric gas/liquid flow rate ratio is 600–700:1 dependent on the amount of ammonia reduction in the process (102). A reduction of at least 95% of the ammonia in the feed is then expected. The main problem encountered is fouling by scaling of salts in the stripper column, mainly carbonates. This problem is resolved by frequent cleaning of the packing material. Alternatively, a water-sparged aerocyclone (WSA) reactor could be used. This has recently been tested for air stripping from wastewater with no evidence of scaling and fouling, probably due to selfcleaning as a result of strong fluid turbulence in the WSA (103). Regardless of the air stripping method, the product made in the absorber unit typically is

ammonia sulfate at a concentration of 28–30%, which can be sold as a fertilizer to agriculture (104–107).

The efficiency of air stripping depends on four major factors: feed pH, feed temperature, ratio of air to feed, and feed characteristics (108,109). The use of lime to raise pH of digested pig manure can lead to precipitation and floc formation. This is unwanted in a stripping column and pretreatment of the slurry after alkalination such as precipitation and sieving is necessary. However, lime is the cheapest alkali source available (discussed later). Further, sieving of suspended solids combined with pH adjustment result in a reduction of total phosphorus (85–93%) and COD (20–48%) in the slurry. This in itself might be of interest as a method for phosphorous recovery (97). In the case of fresh untreated slurry, reduction of total phosphorus was 7.4–12%, and COD (2.8–15%), while in the case of digested manure it was 85–93% and 20–48%, respectively (97). Those lower reduction values for untreated manure might be explained by a higher organic content and lower settling ability of formed flocs (97). Additionally, Zhang and Jahng (110) concluded that using sodium hydroxide or potassium hydroxide is more efficient to raise the pH in piggery wastewater than using lime. Increasing the air flow rate also has a positive effect on ammonia removal due to a decrease of the boundary layer thickness and an increase in mass transfer (111).

At a pH above 11.5 and 22°C, a removal of 90% ammonia (effluent: NH_4-N 0.1 $g \cdot l^{-1}$) in 10 l of swine wastewater (NH_4-N 0.8 $g \cdot l^{-1}$) was accomplished in 7 h when operated in batch mode with an air flow rate equal to 90 $l \cdot min^{-1}$. However, at pH 9.5 and with a flow rate of 45 $l \cdot min^{-1}$, it required 55 h (109). At a lower temperature (15°C), ammonia removal for 1 l of anaerobic digestion effluent (NH_4-N 1.5 $g \cdot l^{-1}$, COD 2.3 $g \cdot l^{-1}$) was 95.3% (effluent NH_4-N 0.04 $g \cdot l^{-1}$) at an air flow rate of 10 $l \cdot min^{-1}$ after 12 h (112). Likewise, Gustin and Marinsek-Logar (113) observed 92.2% ammonia removal efficiency in 2 h from anaerobic digestion effluent (NH_4-N 2.2 $g \cdot l^{-1}$, COD 5.4 $g \cdot l^{-1}$) at 70°C and at pH 10, while at 30°C removal was 80%. On the other hand, Zhang and Jahng (110) reported only 31–70% ammonia removal from piggery wastewater (NH_4-N 5 $g \cdot l^{-1}$, COD 94.2 $g \cdot l^{-1}$) at 37°C and at pH around 10 resulting in effluent with concentration NH_4-N 1.4–3.4 $g \cdot l^{-1}$ under aeration rate 0.5 $l \cdot min^{-1}$ after 24 h. At a higher temperature of 80°C and pH 9.5/11.5, the removal efficiency after 4 h from fresh pig slurry (NH_4-N 3.4 $g \cdot l^{-1}$, COD 70.6 $g \cdot l^{-1}$) was 69% (effluent: NH_4-N 1.05 $g \cdot l^{-1}$, COD 52.2 $g \cdot l^{-1}$) and 98.8% (effluent: NH_4-N 0.04 $g \cdot l^{-1}$, COD 49.4 $g \cdot l^{-1}$), respectively, while from digested pig slurry (NH_4-N 3.7 $g \cdot l^{-1}$, COD 41.2 $g \cdot l^{-1}$) removal efficiencies were almost identical and above 96% (effluent: NH_4-N 0.12 $g \cdot l^{-1}$, COD 32.6–33 $g \cdot l^{-1}$) (97). Similarly, Laureni et al. (108) compared ammonia stripping efficiencies using digested slurries with fresh pig slurry. Removal efficiencies above 90% (effluent: NH_4-N 0.1–0.3 $g \cdot l^{-1}$) at pH 9.5 after nearly 4 h were achieved with slurries with initial low organic content (NH_4-N 1–2.7 $g \cdot l^{-1}$, COD < 10 $g \cdot l^{-1}$). The removal efficiency was lower for slurries characterized with COD above 27 $g \cdot l^{-1}$ (NH_4-N 4.2–6-7 $g \cdot l^{-1}$). This difference is probably due to binding of ammonium ions by organic matter present in the slurry hindering ammonia stripping (114,115). Results reported by Zeng et al. (96) with digested cattle slurry suggest that steam stripping can be operated without preraising pH. This concept is commercially known as the ANAStrip process (116). This can be explained by a high CO_2 content in the digested slurry which is released at high temperature causing a pH increase even though the simultaneous NH_3 release should lead to a pH decrease of the effluent (96). On the other hand, elevated temperatures intensify odor and increase operational costs significantly. It also enhances water evaporation causing a decrease of the ammonia concentration in the effluent. In the case of Zeng et al. (96), a reported decrease from 120 to 30 $mg \cdot l^{-1}$ in the effluent was observed, when the temperature increased from 40 to 80°C. If obtaining a high ammonia concentration condensate is the objective, it is thus advisable to use a feed temperature between 50–55°C (96). The role of raising initial pH is essential when fresh untreated pig slurry is used for air

stripping (97). Similarly, when swine wastewater was used, below pH 10.5, temperature has more influence on ammonia removal than at pH above 10.5 (109).

Raising the pH to 12 or more requires addition of more lime. In the column, this can result in maintenance problems due to calcium carbonate scaling (109). The amount of alkali can be reduced at high temperature due to the higher buffer capacity of manure, which can maintain the desired pH (97). However, one of the biggest challenges is to find cheap energy sources (97). Facilitating ammonia removal can be achieved also by increasing the air flow rate. However, it can also create foaming problems if too much air is introduced to manure and it is an expensive solution as recycling of air or steam is energy intensive (109).

The energy consumption of stripper/absorber plants depend on system design including column type (packed or tray) and heat recovery. For instance, Bauermeister et al. (117) reported electric consumption of 2 kWh/m^3 feed, though when including heating up to 80$°$C the energy consumption increases to 94 kWh/m^3 feed. This shows that heat is the major contributor to the energy consumption. However, Morales et al. (118) and Jiang et al. (104) reported energy consumptions between 200 and 600 Wh/m^3 feed, running the AS process at 35 and 60$°$C, respectively. The estimated electric consumption in this study equals 4.18 kWh/m^3 feed (Table 7) when operating at 50$°$C. This lies between values reported by Morales et al. (118), Jiang et al. (104) and Bauermeister et al. (117). However, the mentioned authors applied packed columns, while in the present study calculations have been made for tray columns. As a consequence, the higher pressure drop encountered in tray columns, resulted in an elevated energy consumption compared to packed columns.

Chemical precipitation

Ammoniacal nitrogen, phosphate, and magnesium (Mg) can be separated from slurry using chemical precipitation. According to Babic-Ivancic et al. (119) both struvite ($MgNH_4PO_4·6H_2O$) and newberyite ($MgHPO_4·3H_2O$) are the main precipitates, newberyite being formed when magnesium is in surplus (Figure 4).

They further reported that coprecipitation could occur in the magnesium-phosphorous concentration region shown in Figure 4. Babic-Ivancic et al. (119) investigated the morphology of the precipitated struvite and found that struvite might precipitate in at least two distinct crystal forms: dendrite and elongated rod. They further found that the dissolution rate constant was roughly one fourth for elongated crystals compared to dendrite crystals. For precipitations from stoichiometric solutions of Mg^{2+}, NH_4+, and $PO_4^{3−}$ at 25$°$C and pH above 8.5, Bouropoulos and Koutsoukos (120) reported precipitation of elongated struvite crystals exclusively. If ammonium is to be removed by precipitation and as a relatively slow release of phosphate and ammonium is desired, struvite precipitation should preferably be conducted using stoichiometric amounts of magnesium and phosphate at pH above 8.5.

As seen from the conditional stability diagram on Figure 5, for most slurry and biogas digestates even though the slurry composition should lead to struvite formation, raising the pH may be advantageous to increase struvite formation and to avoid newberyite formation.

From a practical point of view, Yilmazel and Demirer (121) carried out struvite precipitation from codigested poultry manure and maize digestate. They achieved a 14.6% NH_4^+-N recovery in the struvite without addition of magnesium and phosphate. Lab scale experiments with codigested dairy and poultry manure or swine wastewater achieved a NH_4^+-N recovery in the range of 78–95% by struvite precipitation when additional magnesium and phosphate are added (121–124). In larger scale, this has been tested for phosphate recovery from humane urine (118).
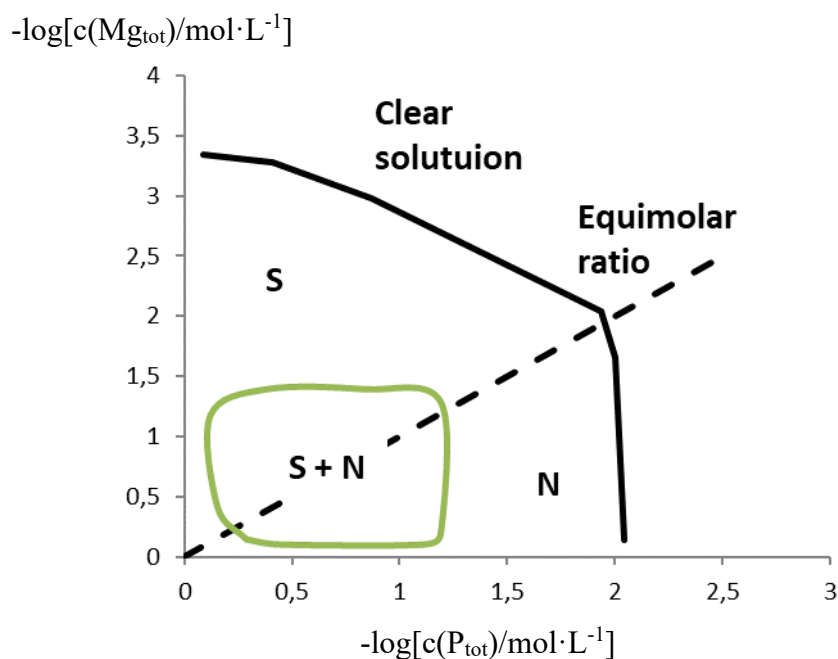
-log[c(Mg$_{tot}$)/mol·L^{-1}]

Figure 4. Precipitation diagram for the system $MgCl_2$-$NH_4H_2PO_4$-$NaOH$-H_2O. Solid line indicates where precipitation will occur, the letters where precipitates of struvite (S) and newberyite (N) will exist (Based on Babic-Ivancic et al. 119).

Generally, in order to achieve high ammonium removal, additional sources of Mg^{2+} (e.g., $Mg(OH)_2$, $MgCl_2$ ·$6H_2O$, MgO, $MgSO_4$, $MgCO_3$, and phosphate, for instance [KH_2PO_4]), have to be added to manure to balance the high ammonium concentrations (123,125,126). Jeong and Hwang (125) concluded that optimal doses of Mg and P are equivalent to around 20% of the initial N content. Lee at al. (126) applied bittern and seawater as alternative Mg^{2+} sources, however it had a negative effect on ammonia removal because of imbalance in the N:P ratio. Optimal conditions for struvite precipitation are pH in a range 9–10.7 and TSS less than 1 g·l^{-1} (122,127).

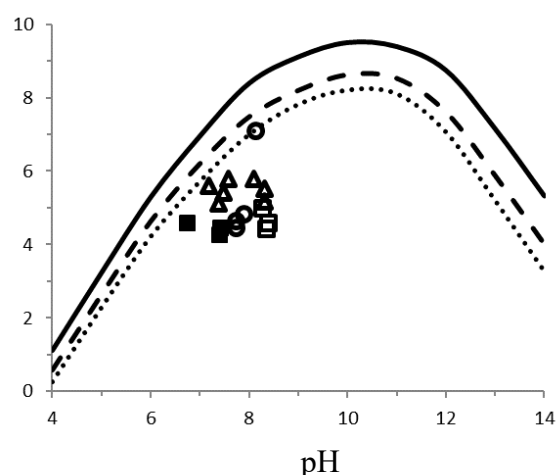Conditional formation constant (logβ)

pH

Figure 5. Conditional stability diagram for struvite formation at different ionic strength – 0M, – 0.1 M, ···· 0.4 M and with the conditional stability coefficients for different slurries: ──── Δ Pig slurry, ○ Cattle slurry, ■ Biogas inlet stream, □ Biogas outlet stream (Based on Sommer and Husted (141)).

Particulate matter in the manure is also a problem. Uludag-Demirer et al. (122) have used screens with 1.19 mm mesh size to remove coarse solid particles from anaerobically digested dairy slurry. Ammonium removal efficiencies were only 56% without removal of TSS from anaerobically digested cattle manure at a PO_4^{3-}/NH_4^+ ratio of 1.25.124 In the case of dairy manure with high amounts of suspended solids rich in phosphorus, microwave (MW) digestion has been implemented to release tied phosphate, ammoniacal nitrogen and metals with efficiencies above 55%. These were then recovered by struvite precipitation.127 This treatment enables discharge of nutrients in soluble form and also reduces TSS, which would else hinder the struvite precipitation process. Radiation combined with adsorption is similar to air stripping, which transfers ammonia from the liquid into the air at high pH, though it includes thermal and nonthermal effects instead of conventional heating. This enhances ammonia removal (127). It has been found that the concentration of released ammonia by radiation increases with increasing temperature, pH, and longer MW radiation time (127,128). Increased heating temperature in combination with H_2O_2 addition also reduces TSS (127). However, hydrogen peroxide addition did not maximize ammonia yield (127). Nonetheless, full-scale implementation of microwave technology for ammonia recovery from manure may be challenging. Similarly to air stripping, increased temperature would require a higher energy input and additionally odor problems may occur. To our knowledge, no full-scale experiments have been conducted and this method requires further development before it can be applied by farmers.

When calcium ions are used as a pH adjuster for a further air stripping step, they also work as precipitants forming $CaNH_4PO_4 \cdot 4H_2O$ (129). This combined concept has been applied by Quan et al. (129) leading to removal of over 91% of NH_3-N. Higher dosage of $Ca(OH)_2$ over $2 \ g \cdot l^{-1}$ at air velocity equals $4.81 \ m \cdot s^{-1}$ resulted in an NH_3-N removal of 94% whereas air inlet velocity over $14 \ m \cdot s^{-1}$ with dosage of $3 \ g \cdot l^{-1}$ of $Ca(OH)_2$ lead to 92% removal.

Chemical precipitation has an advantage over other ammonia removal processes as it is simple to operate. However, the cost is closely related to the price and availability of the chemicals needed and the required product purity. In case of dairy manure, similar to other methods, it requires a pretreatment to remove TSS, leading to a higher investment and operating cost. Additionally, achieving removal of struvite crystals from a mixture of suspended solids depending on the crystal size can be problematic. Therefore, the treated liquid will most likely demand further treatment. The specific gravity of struvite (1.6) only slightly exceeds that of common suspended organic solids (130) and thus centrifugation might be necessary to improve precipitate separation (122). Struvite must also be sterilized and dewatered at 120∘C before applied to fields (131). On the otherhand as reported by Shu et al. (132), recovery of 1 kg of struvite per day is sufficient to fertilize 2.6 ha of crop fields whereas the average application rate of mineral fertilizers per hectare per year is 119 kg N and 39 kg P_2O_5(133).

Ion exchange
Zeolites are inorganic porous materials well known for their excellent adsorption properties for small molecules and likewise their filtering properties even for highly suspended matter effluents (134,135). Ammonium from the liquid manure can be absorbed by a zeolite crystal lattice with a negative excess charge and produce a soil-like material which the authors described to have mold-like consistency (136). The solid fraction containing the zeolites can be separated from the liquid by a decanter centrifuge. The ammonium-zeolite complex is decomposed slowly by the soil bacteria and released to the soil as a nutrient when applied directly to soil (136).

Ammonia removal efficiencies from anaerobic effluent using Ural laumantite were > 99%. However, 1 kg of completely saturated Ural laumantite zeolite contained only 3.6 g of

ammonia, which is too low and uneconomical to be used as a fertilizer (135). Transporting the zeolites to the field will add to process costs and proper regeneration techniques are necessary to improve the economic feasibility of this process (135). Regeneration of the zeolites was suggested by Guo et al. (137) who applied natural clinoptilolite and Na-zeolite on RO permeate of anaerobically digested cattle manure containing nearly 250 mg·l^{-1} of NH_4^+. In this case, regeneration is straightforward. The regeneration cycle consisted of rinsing the zeolite filled column with 50 g·l^{-1} solution of NaCl and 0.2 M of NaOH at flow rates of 2.5–3.3 bed volume (BV)/h for about 2.5 h, followed by washing with 1.2 BV of 0.2 M HCl and 1 BV of deionized water to reach neutral pH.137 Ammonium adsorption capacities by natural zeolite was equal to 0.019 ± 0.002 g·g^{-1} and by Na-zeolite 0.021 ± 0.001 g·g^{-1} leading to 71% ammonium removal efficiency (137). Effective regeneration cycles countered a decrease of ammonia removal capacity and the waste fraction from regeneration needs to be taken into account. A procedure similar to this is used as the final step in full scale at the Kumac Mineralen plant (32) and the Gebrüderen Verkoyen's manure separation plant (34). Milan et al. (138) tested potassic zeolite (K-Zeo), magnesic zeolite (Mg-Zeo), sodic zeolite (Na-Zeo), and calcic zeolite (Ca-Zeo) for ammonia removal from digested piggery manure after screening through a 2 mm sieve. During the first 10 h of operation, ammoniacal nitrogen removal efficiency using Na-Zeo was equal to 91%, while using Ca-Zeo it was 75% (138). However, over the next 10 h, the removal efficiency dropped to 58.3% for Na-Zeo and to 36.7% for Ca-Zeo. Theoretically, Mg-Zeo should facilitate ammonia exchange better than Na-Zeo due to its crystalline structure, though in practice ion exchange is impeded by the high suspended solids content and viscosity of the manure, and competition between Mg^{2+} and Ca^{2+} in the liquid phase (138). Therefore, IE would require pretreatment at least with UF to remove suspended solids before it could be applied and also to avoid clogging of the adsorption column. Ammonia removal is also dependent on the bed height. This is probably due to a combination of liquid dispersion which influence the breakthrough curve for the column and suspended solids removal at the column entrance that would otherwise inhibit the adsorption process (138). Nevertheless, large column heights lead to an increased pressure drop over the column and thus increased operating costs and capital cost of the process. It thus requires careful further analysis to determine the optimal column height to cross sectional area ratio.
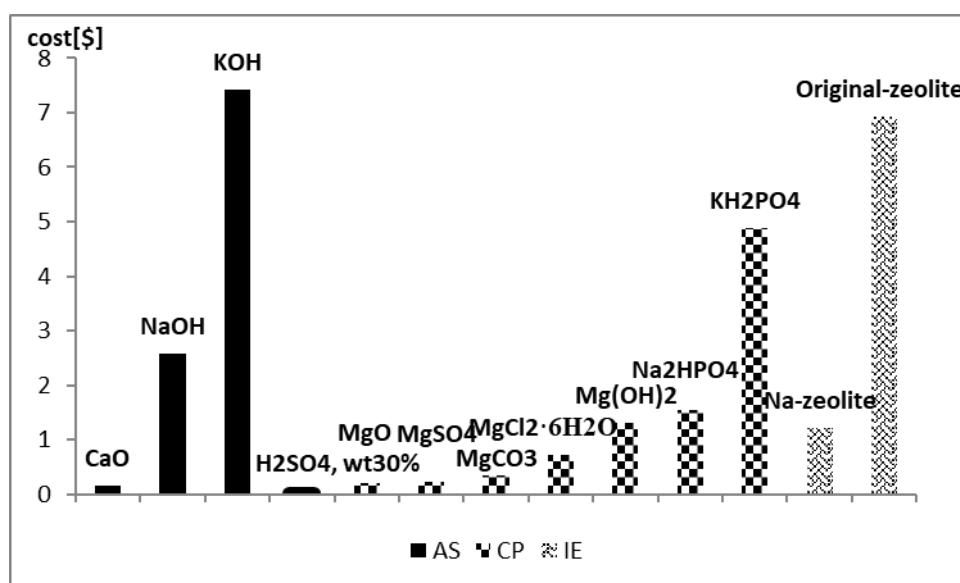

Figure 6. Estimated chemical cost for ammonia removal by physicochemical methods (142).

Table 9 C Procedure for energy consumption calculation of physicochemical methods for ammonia recovery

Air stripping	Chemical precipitations	Ion Exchange
- Liquid flow rate 10 m³/h (118) - Air flow rate 6489.5 m³/h - Column diameter of stripping tray column 1.3 m - Height of stripping column 13.5 m - Sulfuric acid 30 wt% flow rate 0.0023 m³/h - Column diameter of absorber tray column 1.1 m - Height of adsorber tray column 8.9 m - Pressure drop in a stripper has been estimated 13543.8 Pa, and in an adsorber 6771.9 Pa (157) - Fan work (W_f) has been - calculated from $W_f = \eta_f(\Delta v^2/2) + \Delta p/\rho_{air})$ (157) - Fan power (Pf) requirement equals to: $P_f = m_{air}W_f$ (157) - Pump work (W_p) was - calculated from: $W_f = gz + p/\rho$ (157) - Pump power (P_p): $P_p = mW/\eta_p$ (157)	- The mixer height is 1.4 m with diameter 0.95 m - Six-blade turbine with length 0.3 m (158) - Mixing speed 4.16 rps (123) - Power number ($N_p = 6$) (158) - Reaction time 36 min, assuming first order kinetic reaction (124) - Mixer power consumption (P_m): $P_m = N_p n^3 Da^5 \rho$ (158)	- Maximum adsorption capacity for ammonium by Na-zeolite 0.016 g•g⁻¹ (137) - Equilibrium adsorption capacity for ammonium by Na-zeolite 0.004 g•g⁻¹ (137) - Solute feed rate 0.00067 m/s (137) - Diameter of ion exchange 0.26 m and length 2.88 m - Bed volume (BV) 0.155 m³ - Sphericity (_s = 0.57), particle size (dp = 0.5 cm) and porosity (ε = 0.58) (159) - Pressure drop has been calculated using Ergun equation - Breakthrough time 25 h

Comparison of Physicochemical Methods

The physicochemical methods have been compared based on estimated chemical costs (Figure 6) and energy consumption in kWh per 1 kg of ammonia removed. As basis ammonia recovery from 1 m3 of undigested pig manure effluent from UF, containing 1.4 g·l⁻¹ NH₄-N was used (44). Both air stripping and chemical precipitation require prior pH adjustment. Lime is the cheapest pH adjuster compared to sodium hydroxide and potassium hydroxide based on chemical cost alone, though its usage is avoided especially in air stripping due to scaling problems. Alkaline requirements for AS (2.2 kg CaO m⁻³; 6.44 kg NaOH m⁻³, 7.43 kg KOH m⁻³) to raise pH of swine wastewater have been taken from Liao et al. (109) and Zhang et al. (110), while for CP (6 kg NaOH m⁻³) from Ryu and Lee (123).

Total cost of chemicals for AS using sodium hydroxide and 30 wt% sulfuric acid is equal to 3.5 \$/m³feed, whereas the cost is 1.1 \$/m³feed using lime and 30 wt% sulfuric acid. For struvite formation, additional sources of magnesium and phosphate ions are required to balance the ammonia present in the feed. Both magnesium oxide and magnesium hydroxide can at the same time increase solution pH, but as they dissolve slowly in water vigorous mixing and long reaction time is needed (124). Magnesium chloride commonly applied for struvite formation dissolves fast in water, magnesium sulfate slightly slower. A drawback though is that additional alkaline agents are needed to raise pH (124). Even though magnesium carbonate is cheaper than magnesium chloride, it is not advisable for ammonia recovery due to its insolubility in water. As a phosphate source, sodium phosphate dibasic is suggested because it is three times cheaper than potassium phosphate monobasic. Based on this, the total chemical cost for CP including MgCl₂·6H₂O, Na₂HPO₄ and NaOH is equal to 12.9 \$/m³feed. The cost of zeolites for ion exchange is lower compared to the prices on

chemicals for struvite precipitation. The IE process though also requires zeolite regeneration with NaCl (50 g·l^{-1}, 2.5 BV·h^{-1}) and NaOH (0.2 M, 2.5 BV·h^{-1}), followed by washing with HCl (0.2M, 1.2 BV·h^{-1}) (137). Regeneration with NaCl, NaOH, and HCl increases the total cost of chemicals for ammonia recovery to 8.7 \$/m^{3}feed.

To calculate energy requirements of the physicochemical methods for a 95% removal of ammonia from 1 m3 of UF effluent, the assumptions stated in Table 9 had to be made.

The less energy demanding processes are IE, CP, and MD, as the processes consume 0.04, 0.63, and 0.18 kWh/kgNH$_3$, respectively, while AS has the highest energy requirement, almost 3.1 kWh/kgNH$_3$ (Table 7). The MD process is similar to AS, and energy consumption has been recalculated based on ammonia flux and was found to be nearly 18 times lower than for AS (Table 7). Both AS and MD energy consumptions are related to the pressure drop. In the case of MD, optimization can be achieved as mentioned in the membrane processes section by changing from capillary to tubular membranes. In case of AS, using packed columns would lead to a decrease of pressure drop, though the risk of clogging the packing material is also higher.

The operating costs of the physicochemical methods are presented in Table 8. It is concluded that CP with a cost 13.0 US\$/m^3 of feed is the most expensive technology for recovery of ammonia. This is in agreement with Janus et al. (139) conclusions. Ion exchange despite low energy demand is also costly (9.3 US\$/m^{3}feed) because it requires prior suspended solids removal by at least UF and zeolite regeneration. AS seems to be the less expensive (3.8 US\$/m^{3}feed when NaOH is used or 1.4 US\$/m^{3}feed when lime is used). This cost is similar to MD combined with UF (3.7–4.1 US\$/m^{3}feed when NaOH is used or 1.3–1.7 US\$/m^{3}feed when lime is used). In both processes, the chemical costs are the same, as AS and MD require alkaline addition (NaOH or lime) and an absorption solution (e.g., H$_2$SO$_4$). Moreover, it is also found that energy consumption of the blower necessary for AS is similar to the energy consumption of UF necessary for MD. If MD however is applied without UF, then the operating cost is lower: 3.5 or 1.12 US\$/m^{3}feed (if NaOH or lime is applied, respectively). As the ammonia mass transfer is at least 1.5 lower for untreated manure compared to UF treated manure (77), a higher membrane area is required, hence increasing the membrane cost. It is also expected that membranes would demand more frequent cleaning and replacement, because the probability of organic fouling especially by proteins is also higher for untreated manure than for UF treated manure (140).

Summary of physicochemical methods

Most of the physicochemical methods compared to membrane processes are relatively easy to perform and additionally do not require many man hours or much energy. All the processes will be greatly influenced by the presence and nature of particles, SS and organic matter as in the case for membrane processes. Chemical precipitation produces solid products that can be transported over long distances after sterilization and dewatering. In case of ammonium bound to zeolites, transport seems to be rather expensive and a way to regenerate the zeolites is needed for the process to be of enduring usage. Comparing MD with air stripping, which both produce liquid ammonium sulfate, the energy consumption for MD is 18 times lower than for AS. The operating cost of AS though is similar to MD when combined with UF. Running MD without UF pretreatment seems advantageous as this reduces the costs. This prospective advantage though may be more than offset by expenses for membrane replacement and membrane cleaning, as fouling is expected to be a problem for MD, when treating raw manure (140). As information on full-scale running MD plants and long-term operation are presently missing, these factors can at the moment only be inferred.

Air stripping achieves better ammonia recovery (above 95%) for anaerobically digested manure, which is probably due to higher buffering capacity and lower COD. It is advisable in

air stripping to use low temperature and increase pH. This reduces operational costs and odor problems. Too high pH though can lead to scaling problems. The least expensive method to recover ammonia is AS. UF/IE is the most expensive due to the high chemical costs and elevated energy consumption. Furthermore, CP is expensive because of high chemical costs, albeit at the same time it binds phosphorous. This might alleviate the extra expenditure on chemicals, but the obtainable quality of struvite and also treated liquid as well as removal efficiency still calls for more research in order to have a well-known process.

Comparison of ammonia recovery technologies

Table 10 compares the different technologies suggested for the ammonia recovery in terms of best permeate/concentrate quality, ease of maintenance and operational cost.

From a farmer's point of view, the applied technology should be relatively simple to operate, be robust, and require low investment and maintenance costs. In membrane processes, easy, low cost but effective cleaning is very important, and methods without the need of chemicals and subsequent waste handling are highly preferable due to economy and safe operation of the plant. Profitability of membrane processes is also highly dependent upon a necessary feed pretreatment to circumvent fouling and chemical cost to ensure ammonia/ammonium retention. On centralized manure separation plants, RO has proved itself to be a viable process when combined with flocculation, aeration and filtration as pretreatment and IE as posttreatment (31,32). On the farm level when NF or RO is combined with UF as pretreatment, the process requires more energy, based on the calculations presented in this paper. Still compared to the other technologies, it should be less expensive (Table 8). The cost of sulfuric acid to acidify manure is comparable to the cost of UF prior to NF or RO. However, it is expected that membrane cleaning and replacement will be more frequent due to fouling. This increases the total operational cost. Furthermore, from a farmer's point of view running UF prior to NF or RO may be a rather challenging task. Thus, delivering the manure to centralized separation plants could be the preferred solution.

Another promising technology is VSEP NF or RO as the membranes suffer less from fouling during filtration of centrifuged pig manure, compared to other cross-flow NF or RO filtration systems. Unfortunately, the ammonia removal efficiency data for VSEP NF/RO are not reported in literature. Recovery of the original flux of a VSEP NF polyamide membrane, with deionized water alone was possible, as reported by Kertesz et al. (52) Evaluating the process economy would require further work mainly due to lack of ammonia recovery data and energy consumption.

Operating AS or UF/MD is more expensive contrary to UF/NF or UF/RO when NaOH (2.5 US\$/m^{3}feed) is used to increase manure pH, while when using lime (0.1 US\$/m^{3}feed) the cost is similar. However, in the latter case, the risk of scaling in case of AS or fouling in case of MD is also increased due to complex formation between calcium and organics (140). Nonetheless, it should be tested on a long-term basis before implementing the concept on farms. This would allow for optimizing cleaning procedures and simultaneously test the longtime membrane hydrophobicity. Air stripping at low temperatures succeeds in removing 90% of ammonia from raw manure and 95.3% from anaerobically digested manure. Chemical precipitation has a low energy demand but is at the same time the most expensive in chemicals. The treated liquid also needs to be processed further before discharge or reuse as the removal is too low. Moreover, it cannot be applied successfully for dairy manure due to high TSS, which hinders precipitation. Likewise, ion exchange on its own has failed to be a viable technology for ammonia removal, because it is expensive and 1 kg of Na zeolite adsorbed only 21 g of ammonia (137). This is also due to further processing costs of the

regeneration liquid, if the IE adsorbent is to be reused. It is though a viable process as post treatment of RO permeates before discharge to the surroundings (31,32).

Table 10 Comparison of technologies for ammonia removal

Process	Utilities	Complexity equipment	Obtained fraction	Pros	Cons	Operationality at farms	Operaional costs	Uncertanities
Technologies for manure pretreatment								
Sedimentation	Thickener	Periodical cleaning of thickener	TS 4–8 g·l^{-1} (160)	60% removal of TS for slurry with 10–20 g·l^{-1} (160)	5% removal of TS for slurry with 60 g·l^{-1} (160)	Simple	Low	TS removal efficiency depends on initial TS content
Centrifugation	Decanter centrifuge	Initial tests to adjust process parameters such as velocity and retention time	TS 27.7–28.4 g·l^{-1}, COD 31.3–46.7 mg·l^{-1} (161)	High separation efficiency	High power consumption for a high g-centrifuge	Moderate	High	TS removal efficiency depends on initial TS content
Pressurized filtration	Screw press	Regular screw and perforated cylinder cleaning	TS 21.2–42.5 g·l^{-1} (161)	High dry matter content of solid fraction	Ineffective in removing fine solids	Moderate	Low/Medium	Screen blinding
Drainage	Belt separator	Determination the specific filtration resistance in the lab scale for the design full-scale plant	TS 44 g·l^{-1} (21)	Filter cake continuously removed from belt	Particles between 1–100 μm hinder filtration	Simple/Moderate	Low/Medium	Clogging the filter media
Chemical additives prior separation	Flocculants	Testing flocculants efficiency	Flocculation +drainage: TS 21 g·l^{-1} Flocculation +screw press 26 g·l^{-1} (162)	Enhancement of separation efficiency	Toxicity of flocculants	Simple/Moderate	Medium/High	Dosage of flocculants
MF	Pretreatments steel filter 63 μm Membrane: cellulose ester Pump	Air backwashing & chemical cleaning: NaOH & HCl	SS- < 0.2 g·l^{-1}, COD 1–1.5 mg·l^{-1}, BOD 0.3–0.4 g·l^{-1} (38)	Suspended solids has been removed	Inorganic and biofouling	Moderate	Medium	Membrane lifetime
UF	Pretreatment centrifugation Membrane: PVDF, PES Pump	Washing with water	COD ~2 g·l^{-1}, BOD ~0.5 g·l^{-1}, TOC ~0.4 g·l^{-1}, IC ~0.4 g·l^{-1}, TC ~0.7 g·l^{-1} (44)	Suspended solids has been removed	Double ultrafiltration	Moderate	Medium	Membrane lifetime
Technologies for ammonia recovery								
NF	Pretreatment Centrifugation Membrane: VSEP TFC polyamide Pump	Decrease pH below 4.5, Washing with deionized water	TSS removal 93.59% TAN unknown (52)	Reduction total volume of the waste and dry matter, production sanitary water	Need of high pressure	Moderate	Medium	Effect of acidification on membrane lifetime need to be investigated, fouling

Technology	Equipment	pH / Cleaning	Concentrate / removal	Advantage	Disadvantage	Operation	Cost	Challenges
RO	Pretreatment: Vacuum filtration Membrane: Polyamide Pump	Decrease pH below 4.5, Cleaning: water and alkaline	Concentrate TAN 10 g·l⁻¹, Permeate 0.02 mg·l⁻¹ (51)	Concentrate and sanitary water	Need of high pressure	Moderate	Medium	Effect of acidification on membrane lifetime need to be investigated, fouling
ED	Pretreatment: Vacuum filtration Membrane: CMX/AMX Constant voltage 1V Pump	Cleaning with NaOH & HCl	Concentrate TAN 14 g·l⁻¹ (70)	Concentrate and water	Ammonia volatilization, membrane cracked organic fouling	Moderate	Unknown	Capturing volatilized ammonia, fouling
MD	Membrane PP or PTFE Pump	Increase pH above 11, stripping solution	Concentrate TAN 53 g·l⁻¹ (76)	No need of high pressure, pretreatment is optional		Moderate	Medium/High	Effect of alkalization on membrane lifetime need to be investigated, fouling
AS	Stripping tower, pump, compressors	Increase pH above 11, stripping solution	Ammonia removal 90% (97,109,112)	No need of pretreatment	Scaling	Moderate	Medium/High	Scaling prevention
CP	Mg source	Reducing TSS	92% ammonia removal (122)	Binding P at the same time	TSS hinders precipitation	Simple	High	Proper dosage of Mg
IE	Pretreatment: minimum UF Zeolite	Reducing TSS	712% ammonia removal (137)	Adsorption and filtering at the same time	1 kg of Na zeolite retains only 3.6 g of ammonia	Moderate	High	Regeneration procedure, zeolite lifetime

From a farmer's point of view, the applied technology should be relatively simple to operate and require low investment cost.

RO does not fulfill those requirements, since necessary pretreatment makes it expensive. Much better results have been obtained using VSEP NF polyamide membrane, that suffer less from fouling compared to cross flow filtration like NF or RO. To restore the original flux cleaning with deionized water is sufficient. Another promising technology seems to be membrane contactors. As reported by Vanotti et al. *(71)*, it is possible to produce concentrates with TAN 53 g/L without any pretreatment. However, it should be tested on a long term basis before implementing the concept on farms. Air stripping is the biggest membrane rival, removing 90% of ammonia from raw wastes and 96% from anaerobically digested manure at low temperature. The cheapest method and at the same time the easiest is a chemical precipitation. However, it cannot be applied successfully for dairy manure due to TSS, which hinders precipitation. Likewise ion exchange has failed to be viable technology for ammonia removal, since 1 kg of zeolite contained only 3.6 g of ammonia *(91)*.

CONCLUSIONS

From an operational cost comparison (Table 8), it is concluded that at present NF, RO, MD combined with UF, and AS are worth considering to concentrate and recover ammonia fertilizer from manure. AS can produce 28–30 wt% of ammonia sulfate, requiring 3.1 kWh/kg NH3. This will cost 1.4 US$/m³feed or 3.5 US$/m³feed depending on the applied base lime or NaOH (104–107). Among pressure driven membrane processes, energy demands for NF and RO were found to be 2.2 kWh/m³feed and between 4.3–5.5 kWh/m³feed, respectively. Taking into account UF pretreatment for NF and RO, this technology would cost 1.0–1.5 US$/m³feed or 1.2–1-6 US$/m³feed respectively. It is also found that VSEP NF/RO is a promising

technology for ammonia removal due to less proneness to fouling compared to other pressure driven membrane processes. MD has though the potential to become a rival for AS, RO, and NF. The MD cost mainly depends on the alkaline used for raising pH as the energy cost is relatively low. Running the process without UF would cost only 1.1 US$/m^{3}feed compared to 1.3–1.7 US$/m^{3}feed when UF permeate is used as feed. Nevertheless, long-term experiments should be conducted to conclude whether frequent chemical cleaning when treating raw manure would be less expensive than pretreatment with UF. Furthermore, the membrane material and configuration have a large impact on fouling tendency and cleaning efficiency for MF, UF, NF and RO. Therefore, tubular/flat sheet membranes fabricated from highly hydrophilic materials like PA, PSU, MCE, and PVDF should be used. Energy requirement for a 95% removal of ammonia from 1 m^3 of UF effluent is lower for IE (0.04 kWh/kgNH$_3$) compared to MD that requires 0.18 kWh/kgNH$_3$, while CP has a higher energy requirement of 0.63 kWh/kgNH$_3$. Additionally, the total cost of chemicals is estimated for CP to equal 12.9 $/m^{3}feed, for AS 3.5 $/m^{3}feed when NaOH is used or 1.1 $/m^{3}feed when lime is applied and for IE 8.7 $/m^{3}feed. Among all methods for ammonia removal, AS and CP only require prior removal of suspended solids, while all the others require pretreatment with UF followed by cleaning/regeneration cycles.

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