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Potential for pig urine filtration in existing reverse osmosis membrane installations for manure treatment

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NL Next Level Mestverwaarding

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Haalbaarheid van toepassing van `state of the art` omgekeerde osmose installatie voor ontwateren van urine van varkens.

Management Samenvatting

De Membrane Materials and Processes groep (MMP) van de TUe heeft van de industriële partners van het NL Mestverwaarden consortium de vraag gekregen om mogelijkheden te inventariseren voor het concentreren van urine afkomstig van varkens met industrieel verkrijgbare omgekeerde osmose (OO) installaties.

Urine en vloeibare mest bevatten belangrijke mineralen zoals Kalium en Stikstof die worden gebruikt voor bemesting. De concentratie van deze mineralen is echter te laag om direct te kunnen worden toegepast. Ook treden Stikstofverliezen op als gevolg van emissie van ammoniak in de lucht. In dit onderzoek zijn verschillende vloeibare mestsoorten rijk aan voornoemde mineralen geëvalueerd op de mogelijkheid deze eenvoudig te concentreren met OO tot kunstmestvervangers.

De huidige praktijk is om drijfmest te vergisten tot methaan, gevolgd door een vast/vloeistof scheiding van het digestaat met decanters of bandfilters. De vaste fractie wordt dan gebruikt als bodemverbeteraar terwijl de mineraal houdende fractie kan worden ingezet als meststof. Een andere route is om direct te starten met een scheiding van de vaste en vloeibare fractie waarbij een meststof rijk aan organische stof wordt verkregen en een vloeibare minerale fractie. Om de waarde van het mineraalconcentraat te verhogen is het gewenst een hogere concentratie te bereiken dan nu mogelijk is. Hiermee wordt de actieradius voor transport van het product vergroot. In beide routes hierboven beschreven is de voorbehandeling van de mest voor OO essentieel.

Het grootste probleem tijdens verwerking van drijfmest (urine + feces) is de vorming en vrijkomen van ammoniak naar de atmosfeer. Wanneer urine en feces separaat worden opgevangen (en dus niet met elkaar in contact komen), zal geen vorming van ammoniak optreden, waardoor emissie van ammoniak naar de atmosfeer sterk k wordt gereduceerd. Bij gescheiden opvang van urine en feces zullen de individuele stromen dan ook apart moeten worden verwerkt. In veel bestaande mestverwerkingsinstallaties is de laatste processtap het ontwateren van de mineralenstroom waarbij “loosbaar “ water wordt geproduceerd. In het geval van Mestscheiding bij de bron zal de voeding van de installatie urine zijn i.p.v. mest waarbij het doel hetzelfde is: mineraal concentratie en productie van “loosbaar” water.

Doel van deze studie de mogelijkheden en beperkingen voor de toepassing van bestaande OO-installaties te onderzoeken voor de productie van “loosbaar” water en hoogwaardige vloeibaar N, K-concentraat uit varkensurine. Deze studie is gebaseerd op een analyse van de beschikbare literatuur, aangeleverde samenstelling van verschillende urinefracties en filtratie experimenten op lab schaal met verschillende urine en mestfracties.

In het literatuurreview worden de factoren beschreven die de effectiviteit van urinefiltratie door OO beïnvloedden: 1 osmotische druk van de voeding; 2 aanwezigheid van ureum, ammoniak en ammonium; 3 vervuiling; 4 prestatie (flux) van OO-membranen voor urinefiltratie.

Vervolgens werden de resultaten van de lab schaal experimenten geëvalueerd m.b.t filtreerbaarheid van de verschillende urine/mest monsters. De volgende 4 stromen zijn beschouwd:

1. Zuivere urine afkomstig van vleesvarkens
2. Urine afkomstig van een transportband, vervuild met vaste mestdelen
3. Dunne mestfractie na een mechanische scheiding, voeding van OO
4. Dunne digestaatfractie na een mono-vergister en scheider

De belangrijkste conclusies;

Silt density Index (SDI) en voorbehandeling

Zelfs verse zuivere urine bevat al neerslag en vaste delen die resulteren in een SDI van 3 tot 4. Hoewel verwerking middels OO mogelijk is, geven deze waarden aan dat aanzienlijke vervuiling zeer waarschijnlijk zal optreden en dat frequente reiniging van de membranen nodig zal zijn. Door de instabiliteit van de urine wordt verwacht dat vervuiling nog ernstiger zal worden wanneer de urine minder vers is of vervuild met feces, wat in het praktijk veelvuldig zal voorkomen. In die gevallen zal toegenomen vlokvorming en sedimentatie van vast materiaal leiden tot snellere en meer vervuiling met als gevolg een sterkere afname van de waterproductie. Consequentie hiervan is dat ook zuivere urine een voorbehandeling nodig heeft om grotere deeltjes en vlokken te verwijderen. Mogelijk leidt deze verwijdering van de grovere vaste delen weer tot een ander soort vervuiling door vorming van een dunnere maar compactere “vervuilingskoek” door de “kleinere” deeltjes die resteren na de voorbehandeling.

Concentratie factor

De maximale concentratiefactor van een mineralenconcentraat hangt af van de effectieve transmembraandruk: het verschil tussen de druk over het membraan en de osmotische druk van de mineralenstroom (de voeding). Hoe hoger de concentratie mineralen (deeltjes en ionen) in de mineralenstroom hoe hoger de osmotische druk zal zijn. Een goede maat voor de osmotische druk is de geleidbaarheid van het concentraat. De meeste mestverwerkingsinstallaties gebruiken een voedingsdruk van ca 40 bar in de eerste trap waarbij een concentraat wordt gemaakt met een geleidbaarheid van 50mS (concentratie factor 2 à 3). Aangezien de geleidbaarheid van zuiver urine vergelijkbaar is met die van drijfmest wordt geschat dat de maximale concentratiefactor van urine ook 2 à 3 zal zijn.

Vervuiling

In de literatuur wordt veelvuldig gesproken over het optreden van vervuiling door calcium, magnesium en silica tijdens OO. Met name bij hoge concentratiefactoren (en dus hoge concentraties), worden de lokale concentraties van bovengenoemde componenten vlak bij het membraan zeer hoog: ze worden immers tegengehouden. Hierbij kunnen concentraties worden bereikt die hoger zijn dan de oplosbaarheid waardoor neerslag plaats zal vinden op het membraan. Uit een eerdere studie met OO van voorbehandelde drijfmest in industriële installaties bleek m.n. silicavervuiling op te treden met flinke reducties in flux tot gevolg. De WUR heeft het Silica gehalte in de onderzochte stromen bepaald waaruit bleek dat de Silica concentratie in urine hoger is dan die in mestwater waardoor de verwachting dat Silica scaling ook tijdens OO-filtratie van urine zal optreden zeer aannemelijk is, overigens in het onderzochte digestaat werd een nog hogere silica waarden gevonden.

Stabiliteit van de voeding van de OO-installatie

Tijdens de experimenten op lab schaal werd snel duidelijk dat de zuivere urinemonsters niet stabiel zijn in de tijd. Zelfs tijdens opslag in de koelkast neemt de troebelheid van de monsters door vlokvorming en sedimentatie iedere dag toe wat in de experimenten resulteerde in een hogere mate van vervuiling. Het wordt daarom aanbevolen om de urine direct na opvang te verwerken.

Flux waarden (capaciteit)

De fluxwaarden die in de praktijk realiseerbaar zijn kunnen niet worden afgeschat op basis van de weinige literatuurgegevens die beschikbaar zijn over urinefiltratie. Waarden die worden gerapporteerd zijn orde grootte van 2-6l/m2/h bij 10 bar. Gerapporteerd wordt ook dat er sprake is van grote verdamping van ammoniak en co-permeatie van ureum wat een negatief effect heeft op de waterkwaliteit van het permeaat (en dus op de loosbaarheid van het permeaat). Ter vergelijking: een industriële OO-installatie die drijfmest verwerkt heeft een flux van ca 9 l/m2/h bij 40 bar.

Samenvattend: de werkelijk flux die kan worden gehaald in een specifieke situatie is sterk afhankelijk van de kwaliteit van de voeding, de toegepaste voorbehandeling, gebruikte additieven bij de voorbehandeling en de procescondities tijdens filtratie maar het lijkt er niet op dat de flux tijdens filtratie van zuivere urine veel hoger zal zijn dan die van goed voorbehandelde drijfmest.

NH3 emissie en verlies van ureum naar het permeaat

Ureum wordt door het enzym urease dat aanwezig is in feces omgezet in ammoniak (NH_3) dat in water in evenwicht is met ammonium (NH_4^+). Er wordt geen NH_3 gevormd wanneer feces en urine apart worden verzameld. In drijfmest is NH_3 in evenwicht met NH_4^+. De pKa van NH_4^+ is 9.2, wat betekent dat bij een pH van 9.2 de verhouding NH_4^+/NH_3 =1. Bij lagere pH-waarden neemt de concentratie NH_4^+ toe t.o.v. NH_3. Tijdens OO zal het ongeladen NH_3 makkelijker door het membraan permeëren dan het geladen NH_4^+. Om het evenwicht te herstellen zal daarom in het concentraat (de voedingskant van het membraan NH_4^+ worden omgezet naar NH_3. Bij een lagere pH van de urine zal bij een OO-proces de emissie van NH_3 lager zijn zowel tijdens het proces als ook tijdens opslag. Bij gescheiden opvang van feces en urine wordt het ureum niet omgezet in NH_3 (en NH_4^+) het nadeel is echter dat ureum een klein ongeladen molecuul is dat minder goed door het OO-membraan wordt tegengehouden en dus in het permeaat (loosbaar water) terecht komt. Een aanvullende behandeling van dit permeaat zal dan nodig zijn om het permeaat te mogen lozen.

1. Executive summary

The industrial partners of NL Next Level Mestverwaarding asked the Membrane Materials and Processes group of Eindhoven University of Technology to perform an inventory of the potential of existing reverse osmosis (RO) installations in manure treatment for the dewatering of pig urine.

Liquid manure contains important minerals such as potassium and nitrogen that are used for crops fertilization. Before this liquid manure concentrates can be applied there are several hurdles to take. The most important ones are the low mineral content in the liquid fraction and the loss of reactive nitrogen in the form of ammonia and urea to the atmosphere. In this research manure mineral sources from different origin are evaluated on their on their ease and simplicity of concentrating them into useful artificial fertilizer substitutes. The current state of the art is manure digesting to produce methane followed by solid /liquid separation using decanters of belt filters. The solid fraction is used as soil improver while the mineral containing liquid fraction is used as fertilizer. The other route is to start with solid/liquid separation to produce an organic solid fertilizer and a liquid mineral concentrate. To increase the economic value of the mineral concentrate it has to be concentrated which increases the distribution radius. Pretreatment before RO filtration is essential in both routes.

The major issue in manure (urine and feces combined) treatment is the formation and release of ammonia to the atmosphere thus increasing nitrogen emissions. When urine and feces would be collected individually, ammonia formation will not occur, significantly reducing nitrogen emissions. This implies that, instead of manure processing, further urine processing is required. The final treatment step in many existing manure treatment installations is the dewatering to produce water that meets the specifications for discharge. Instead of feeding ‘manure’, the idea would be to feed urine to the existing RO installation with the same goal.

The specific aim of this study was to investigate the possibilities and limitations for the use of existing RO installations to produce clean water ready for discharge and a high-quality, liquid N,K-concentrate from pig urine. Following the proposal (dd. 9 November 2020), the study is based on available literature, composition data of different urine fractions supplied by the consortium and lab scale filtration experiments with different urine and manure fractions.

The report first starts with a literature overview of the factors affecting the potential of urine filtration in RO. This is subdivided in 1) reverse osmosis and osmotic pressure of the feed solution; 2) Urea, ammonia, ammonium, and reverse osmosis; 3) Scaling; 4) RO membrane performance for urine filtration. Next, the experimental work to practically evaluate the filterability of different urine/manure samples is evaluated. In this experimental part, four different streams are considered:

1. Pure urine from fattening pigs
2. Contaminated urine from a conveyer belt
3. Thin manure after mechanical separation, feed RO
4. Thin digestate after mono-digester and separator

The major conclusions of the evaluation can be subdivided in the following aspects:

SDI and pretreatment

Even freshy delivered urine contained already some flocs and solid material resulting in an SDI value between 3 to 4. Although RO operation is possible in such cases, these SDI values also clearly indicate that particulate fouling is likely to be a problem and regular cleaning is necessary. Due to the very limited stability of urine in time, this is even more severe in cases where collected urine is not immediately used in the RO. In such cases increased flocculation and sedimentation of solid material increases the amount of solid material in the feed resulting in increased fouling and an expected strong decrease in flux as well. As a consequence, also pure urine will need pre-treatment to remove larger particles and flocs. However, this may also impact the nature of the fouling layer as smaller particles may form a denser, more compact cake layer.

Concentration factor
The concentration factor of the mineral concentrate that can be reached depends on the effective transmembrane pressure which is the difference between the hydrostatic pumping pressure and the osmotic pressure of the mineral (liquid manure) stream. The osmotic pressure of a solution is related to the amount of particles and ions present in the solution and is therefore related to the conductivity of the solution. In most manure treatment plants the applied pumping pressure is approx. 40 bar in the first RO stage, which results in a concentrated stream with a conductivity of 50 mS (concentration factor 2 - 3). Since the conductivity of pure urine is comparable to that of thin manure it is estimated that also the maximum concentration factor for urine is 2 - 3.

Scaling
Literature extensively reports the occurrence of calcium, magnesium, and silica scaling in RO applications. Especially at high concentration factors, local concentrations of these components close to the membrane surface can reach very high values close to or even above the solubility product values of the respective components. From our previous study with pretreated manure RO filtration, especially serious silica scaling resulting in severe flux decreases was regularly observed in several industrial installations. Whether this will play a role when using urine in existing RO installation cannot yet be predicted as compositional analysis of supplied urine fractions is still in progress (WUR).

Stability of the feed
During the experiments performed, it was clearly observed that especially the urine samples were not stable in time. With increasing time, the turbidity of these samples increased every day although the samples were stored in a fridge at 4 °C. Flocculation and the deposition of solid materials seemed to occur resulting in higher membrane fouling tendency of the feed. Therefore, it is highly recommended to treat urine directly after collection.

Flux values
The flux values that can be obtained in practice are very hard to predict based on the only very few literature data reported on urine filtration. The very few studies on this topic present values in the order of 2-6 l/m^2 h 10 bar (= 0.2 - 0.6 l/m^2 h bar). Researcher however also report severe evaporation of ammonium and co-permeation of urea compromising the product water quality. For comparison, the RO installation at a reference Farm (III) (manure treatment) produces fluxes in the range of about 9 l/m^2 h 40 bar (= 0.1-0.2 l/m^2 h bar). Overall, actual fluxes that can be obtained in a specific situation are highly dependent on e.g. the supplied feed quality, the applied pre-treatment, used additives and applied conditions.

NH_3 emission and urea losses to the permeate fraction.
Urea is converted in ammonium (NH_4^+) by the enzyme urease which is present in the feces. When the feces and urine are collected separately no NH_4^+ will be formed. In liquid manure NH_4^+ is in equilibrium with ammonia (NH_3). The pKa of ammonium is 9.2 this means that at a pH of 9.2 the ratio NH_4^+ NH_3 is 1. At lower pH values the equilibrium is in favor of the NH_4^+. During the concentration in the RO process the NH_3 permeates the membrane. As a consequence, NH_4^+ is converted to NH_3 in order to re-establish the equilibrium. Therefore, operation at lower pH is beneficial to lower the NH_3 exhaust from the system (and storage). However, a newly emerged major disadvantage of separate collection of feces and urine is that now the nitrogen is present as urea which retention by RO membranes is very limited and will therefore end up in the discharged water requiring an additional post treatment to fulfill the environmental discharged regulations.

2. Research scope

2.1 Introduction

The industrial partners of NL Next Level Mestverwaarding asked the Membrane Materials and Processes group of Eindhoven University of Technology to perform an inventory of the potential of existing reverse osmosis (RO) installations in manure treatment for the dewatering of pig urine.

The major issue in manure (urine and feces combined) treatment is the formation and release of ammonia to the atmosphere thus increasing nitrogen emissions. When urine and feces would be collected individually, ammonia formation will not occur, significantly reducing nitrogen emissions. This implies that, instead of manure processing, further urine processing is required. The final treatment step in many existing manure treatment installations is the dewatering to produce water that meets the specifications for discharge. Instead of feeding 'manure', the idea would be to feed urine to the existing RO installation with the same goal.

2.2 Aim of this study

The specific aim of this study was to investigate the possibilities and limitations for the use of existing RO installations to produce clean water ready for discharge and a high-quality, liquid N,K-concentrate from pig urine. Following the proposal (dd. 9 November 2020), the study is based on available literature, composition data of different urine fractions supplied by the consortium and lab scale filtration experiments with different urine and manure fractions. This report describes the results obtained in this study.

2.3 Approach

Detailed compositions of pure urine, impure urine originating from a conveyer belt, thin manure after mechanical separation and thin digestate after mono-digester and separator will be provided by the consortium. Components include N-, P-, K-, Si-components, macro- and micronutrients, conductivity, organic and inorganic C, pH, solids fraction. Based on these compositions, TU/e will perform a literature study on the potential applicability of urine as feed for existing RO installations describing opportunities and limitations in terms of pretreatments, fluxes, concentrations, and operational conditions.

Next, also 2 liter of each of the 4 fractions will be supplied and TU/e will experimentally investigate the filterability of these fractions and compare the filterability of the urine fractions to that of the manure streams.

2.4 Structure of this report

The report first starts with a literature overview of the factors affecting the potential of urine filtration in RO. This is subdivided in 1) reverse osmosis and osmotic pressure of the feed solution; 2) Urea, ammonia, ammonium, and reverse osmosis; 3) Scaling; 4) RO membrane performance for urine filtration.

Next, the experimental work to practically evaluate the filterability of different urine/manure samples is evaluated. In this experimental part, four different streams are considered:

1. Pure urine from fattening pigs
2. Contaminated urine originating from a conveyer belt
3. Thin manure after mechanical separation, feed RO
4. Thin digestate after mono-digester and separator

Finally, the report is concluded with an overview of the insights, conclusions and recommendations obtained during this study.

3. Factors affecting the potential of urine filtration in RO

3.1 Introduction

Based on literature research the following factors that impact the potential of RO for the treatment of urine to produce clean water were identified:

1) Reverse osmosis and osmotic pressure of the feed solution
2) Urea, ammonia, ammonium, and reverse osmosis
3) Scaling
4) RO membrane performance for urine filtration

In the following paragraphs first the theoretical aspects and implications of item 1, 2 and 3 will be discussed. This is followed by a literature overview of urine dewatering using membrane-based processes with a strong focus on reverse osmosis. This chapter is concluded with a description of the implications of these aspects for the filtration of urine using existing RO installations.

3.2 Reverse osmosis and osmotic pressure of the feed solution

RO is a pressure driven membrane process in which a pressure (ΔP) higher than the osmotic pressure ($\Delta\pi$) of the feed is applied to induce water permeation through a semi-permeable membrane (figure 1). The membrane allows water to permeate while ions (salts) are retained. The permeate (clean water) has a low ion concentration, the retentate (concentrate) has a high ion concentration.

The osmotic pressure of a solution (e.g. urine) is directly dependent on the concentration of ions and molecules in that solution, following equation 1:

$$Osmotic\ Pressure\ (\pi) = [\Sigma(N \cdot C)] \cdot R\ \cdot T \qquad (1)$$

Where:
N = Number of dissolved particles [-]
C = Concentration [mol L^{-1}]
R = universal gas constant [= 0.0810 L bar mol^{-1} K^{-1}]
T = temperature [K]

When the applied feed pressure is lower than or equal to the osmotic pressure of the solution to be treated, water permeation will not occur. Only when the applied pressure exceeds the osmotic pressure, clean water can be produced (Figure 2). So in order to use urine as RO feed, the applied pressure should well exceed the osmotic pressure of urine. As not much literature on pig urine filtration is available in literature, for comparison, human urine has an osmolality of 500 – 850 mOsmole/L which corresponds to an osmotic pressure of 12 – 21 bar [1]. For water permeation, the applied pressure in this case should thus be higher than this value.

This also sets limitations in terms of the concentration factor that can be obtained: when the osmotic pressure of the concentrated feed reaches the applied mechanical pressure, water permeation will no longer occur and clean water production stops.

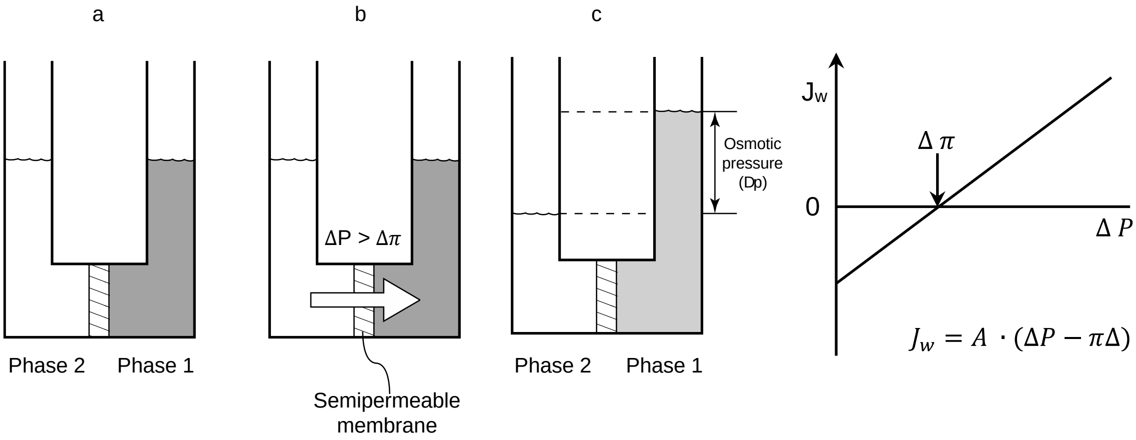

Figure 1: Schematic drawing of osmosis and the water flux (J_w) as a function of the applied mechanical pressure [2].

3.3 Urea, ammonia, ammonium, and reverse osmosis

In the presence of urease (present in feces), after excretion, urea ($CO(NH_2)_{2(aq)}$) in urine can converted to ammonia (NH_3). This process is highly dependent on temperature and time. Below 0 ^{O}C the pH of urine is rather stable. At or above room temperature the pH of urine changes following reactions 2 and 3:

$$CO(NH_2)_{2(aq)} + H_2O_{(l)} \xrightarrow{\text{Urease (@25deg.C)}} NH_3 + NH_2COOH_{(aq)} \tag{2}$$

$$NH_2COOH_{(aq)} + H2O_{(l)} \longrightarrow NH_{3(aq)} + H_2CO_{3(aq)} \tag{3}$$

Without urease (the catalyst) and below 25 ^{o}C this reaction is very slow taking 80 years but within the presence of urease the reaction is completed within 40 minutes [3]. Since urease is mainly present in the feces, separate collection of feces and urine would be advantageous in livestock farming to minimize the NH_3 exhaust from pig houses and stables. The form in which the formed ammonia is present is highly pH dependent (figure 2) [4].

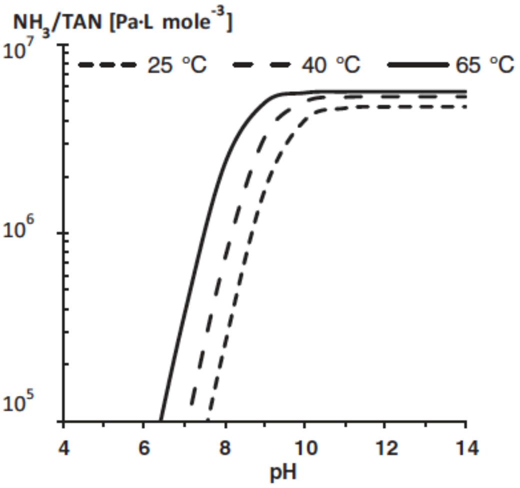

Figure 2: Influence of pH and temperature on the partial pressure of NH_3 [4].

At pH values between 4 and 7, all ammonia dissolves in the liquid phase forming NH_4^+ (reaction 4), but above pH 9.3, almost 50% the ammonia dissolved in the liquid phase is converted into gaseous ammonia which is released from the liquid to the atmosphere according (reaction 5).

$$NH_{3(aq)} + H^+ \xrightleftharpoons{pKa=9.25} NH_4^+ \quad (4 < pH > 7) \tag{4}$$

$$NH_{3(aq)} \rightleftharpoons NH_{3(g)} \quad (7 < pH > 9.5) \tag{5}$$

Only at low pH, ammonia evaporation can be suppressed. For example, Cahn et al. [5] collected separately pig feces and urine. The pH of the urine was dependent on the type of pig feed and varied between 6.4 and 7.0 (average value: 6.8 +/- 0.2). The nitrogen in the urine fraction was almost completely present as urea whereas only 4.5% was present as NH_4^+. To prevent evaporation of ammonia the urine was collected in sulphuric acid keeping the pH below 2. Although the concentration of nitrogen in the feces was 50% higher than that in the urine in total 75% of the N present was excreted via the urine.

The total ammoniacal nitrogen present in manure is defined as the total of nitrogen present as ammonia (NH_3) and ammonium ions (NH_4^+). Ammonia can freely permeate dense RO and NF membranes, whereas ammonium ions in solution are actually retained by the membranes due to lose complex formation with anions in the manure such as HCO_3^-, PO_4^{3-}, and VFAs [6]. For this reason often a pH adjustment to lower the pH of the solution is applied before in order to retain the ammonia as NH_4^+.

Lee et al. [7] compared seven candidate RO membranes using a stirred cell (batch operation) to determine the membrane flux and the solute rejection for synthetic space mission wastewaters where wastewater A contained nitrogen in the form of urea and creatine, while wastewater B contained nitrogen as NH_4^+ (figure 3).

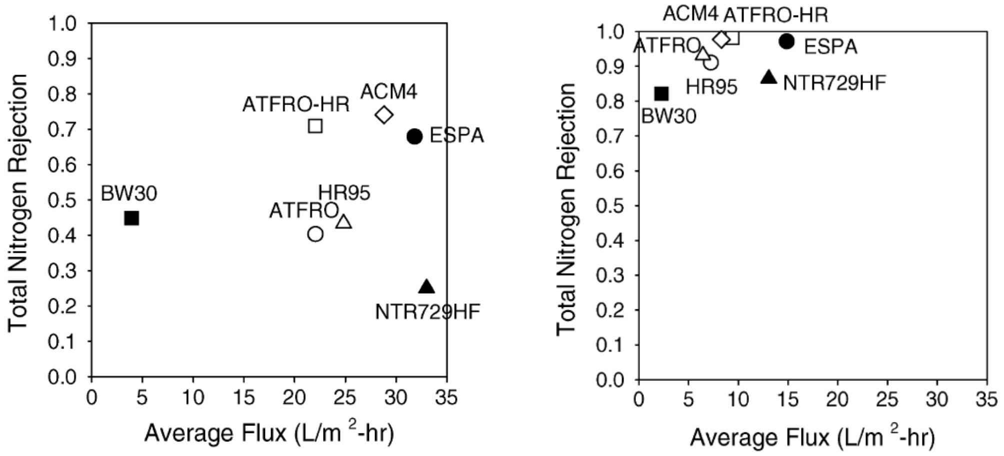

Figure 3: Total nitrogen rejection by different RO membranes with synthetic wastewater containing A) urea and creatine as nitrogen source (left) and wastewater B containing $NH4^+$ as nitrogen source (right). Operating conditions: 800 kPa, stirring speed: 400 rpm, salt concentration: 0.02 M, 60% recovery [7].

Data were obtained in a small-scale setup with artificial feeds not representing real feed streams. However, interestingly, the researchers found that even through urea is larger in size than ions such as Na^+, Cl^- and NH_4^+, its rejection is significantly lower due to fact that charge interactions between charged ions and the charged membrane interactions are more important than size exclusion effects.

In an additional study [8] Lee et al. compared the filtration and retention behavior of different nitrogen compounds using low pressure RO (LPRO), RO or NF. The corresponding retention values are tabulated in table x and figure x gives a graphical representation of these values.

This table clearly shows that where membrane retentions for salts are high due to charge-charge interactions, urea shows very low retentions and is a difficult component to retain by an RO membrane. Even though the size of the urea molecule is one of the biggest among all the components listed in table 1, its retention is by far the lowest. This is even more striking knowing that the effective diffusion coefficient of urea is with $13.8 \cdot 10^{-10}$ m^2/s comparable to that of the other components in table 1, with exception of creatine which has an effective diffusion coefficient of a factor 2 lower, i.e. $6.6 \cdot 10^{-10}$ m^2/s.

Table 1: Nitrogen compounds present in animal waste, hydrated solute radius from the cation and anion species and the retention for nanofiltration, low pressure (LP) RO and brackish water RO membranes. The feed concentration is 250 mg N/L and the applied pressure is 8 bar. Data abstracted from [8].

Component	**Solute radius [nm]**	**NF NF-45 DOW Filmtec**	**LPRO ESPA Hydranautics**	**RO ATFRO-HR AMT**
Ammonium chloride	0.11 0.11	28.9	91.8	93.3
Urea	*0.24*	*19.8*	*52.2*	*50.0*
Ammonium formate	0.11 0.15	64.5	87.3	90.3
Sodium nitrite	0.16 0.11	40.5	88.1	86.6
Sodium nitrate	0.16 0.24	24.8	87.3	88.8
Ammonium carbamate	0.11 0.17	75.2	85.1	87.3
Ammonium carbonate	0.11 0.24	70.2	85.8	86.6
Creatinine	0.33	90.1	95.5	98.5

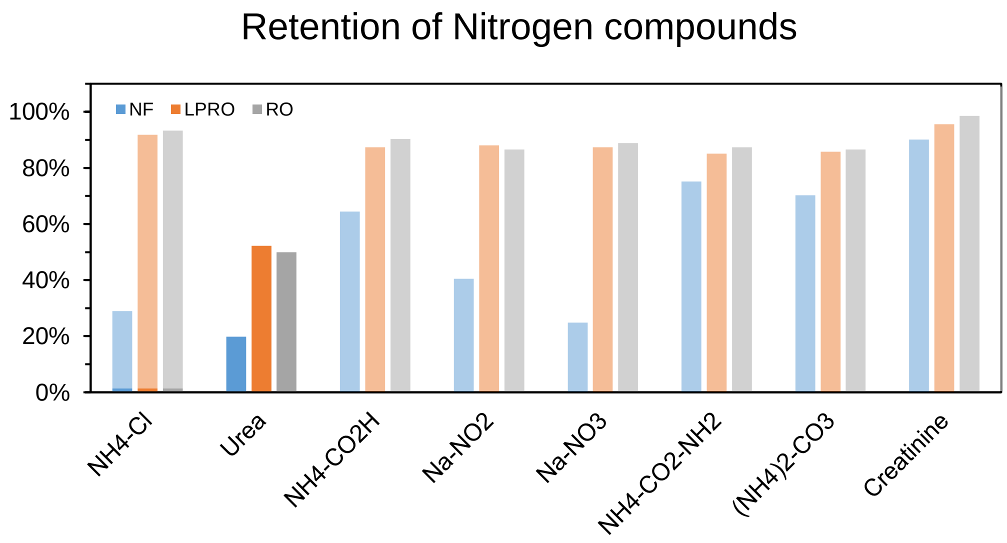

Figure 4:Graphical representation of the data presented in table 1.

Lee et al. also determined experimental rejection values of nitrogen in different forms and calculated the theoretical effect of the ratio of ammonium to urea in the feed on the rejection in RO, LPRO and NF (figure 5).

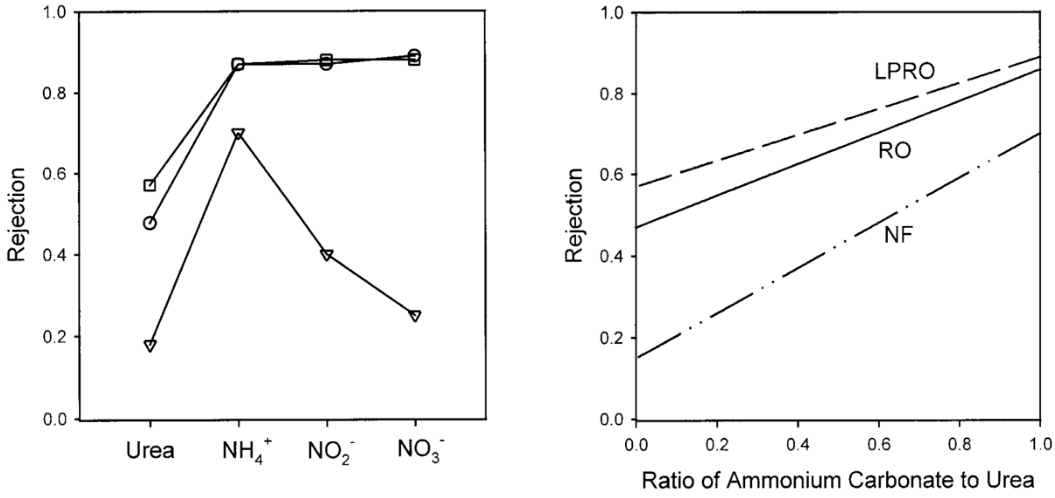

Figure 5: Left: effect of nitrogen form on experimentally measured rejection of urea, NH_4^+ (ammonium carbonate), NO_2^- (sodium nitrite), and NO_3^- (sodium nitrate). Experimental conditions: 800 kPa, stirring speed: 400 rpm, feed concentration: 250 mg N/liter. Right: theoretical estimate of the dependence of rejection on the ratio of ammonium carbonate to urea at similar conditions [8].

Both figures clearly show that rejection of N strongly decreases when this is present as urea. Moreover, the positively charged ammonium ion shows high rejection values in RO. Correspondingly, with increasing urea amounts the ratio ammonium carbonate/urea decreases resulting in an overall decrease of rejection of N.

3.4 Literature overview of RO membrane performance for urine filtration

3.4.1 Reverse osmosis for animal urine concentration

Concentration of urine is not well described in literature. Humane urine is an exception since separate collection of human excretion products is much easier than separate collection of feces and urine from animals. As only very few articles describe the separate collection and processing of animal excretion also literature on the treatment of human urine is included.

Willers et al. described a process where the feces of pigs are composted while the urine fraction is concentrated using water evaporation. In this process exhaust air from the pig house is led through a nitric acid acidified packed bed scrubber. Water evaporation produced a concentrated N/K fertilizer while simultaneously removing the ammonia from the pig house exhaust air [9]. The ammonia scrubbing efficiency and the evaporation rate were determined during one pig fattening round of 112 days. A concentration factor of 7 could be obtained where the ammonia scrubbing efficiency of the process varied between 95 and 65% and decreased at higher salt concentration. The N,P,K concentrations in the concentrated urine fraction show a significant increase relative to their counterparts in the native urine, with especially a strong concentration increase of nitrogen (table 2).

Table 2: Concentration of native pig urine and the concentrated urine fraction after treatment in an evaporative packed bed scrubber.

Component	**Nitrogen**	**Phosphorus**	**Potassium**
Collected native urine [g/kg]	4.4	0.03	6.6
Concentrated urine fraction [g/kg]	91.3	0.2	46.5

Mondor et al. [10] aimed at producing a concentrated nitrogen fertilizer from liquid swine manure using electrodialysis (ED) as pretreatment followed by an RO concentration step. ED is an electro membrane process in which an electrical potential is used to separation charged ions. In the ED pre-treatment the maximum total ammonia concentration (NH3–N) that could be obtained was limited by water transport from the manure to the concentrate compartment, and ammonia volatilization (17%) from the open concentrate compartment. A maximum total NH3–N concentration of ˜16 g/L was achieved.
Treatment of ED concentrate with an NH3-N concentration of 8.7 g/L in an RO (table 3) showed that the RO permeate accounts for 49.6% of the initial volume and contained 8.6% of the ammonia. However, the RO concentrate contained only 66.6% of the initial total NH3–N, indicating evaporation of 21.2% of the ammonia. The ammonia concentration in the RO concentrate obtained was approximately 13 g/L, which is similar to the maximum concentration that could be achieved by ED. So, although the use of ED and RO to recover and concentrate ammonia might be potentially interesting, evaporation of ammonia due to the higher pH values reduces its applicability significantly.

Table 3: Characteristics of the ED concentrate fed to the RO and the obtained compositions of the RO permeate and concentrate [10]

Parameter	ED concentrate		RO permeate			RO concentrate		
	Concentrate (mg/L)	Mass (g)	Concentrate (mg/L)	Mass (g)	Initial (%)	Concentrate (mg/L)	Mass (g)	Initial (%)
Dry matter	19 645	164.0	1164	4.8	2.9	40 511	151.3	92.3
Volatile matter	4745	39.6	181	0.8	1.9	11 130	41.4	98.3
NH_3–N	8743	73.0	1508	6.2	8.6	12 839	48.6	66.6
Alkalinity (as $CaCO_3$)	31 000	258.9	5364	22.2	8.6	43 000	162.8	63.9
pH	8.4		9.8			8.9		

Thörneby et al. [11] concentrated liquid effluent (urine) from three different sources. Wastewater obtained from three different sources were used: Farm A (dairy and raising heifers), Farm B (pig farrowing), and Farm C with about 1000 fattening pigs. Wastewaters from Farm A and B were immediately drained using perforated iron plates and the solids were removed twice per day. At Farm C feces and urine were collected and stored together in a large tank without cover. The liquid fraction from the slurry was separated, either by a screw separator, or by sedimentation before RO operation. The original conductivity of the fresh pig urine varied between 270 and 700 mS/m while that of the heifers was 2400-2650 mS/m. All samples were stored in a storage tank prior to filtration. During transport to storage the concentration decreased due to recombination of urine with wastewater by about 50% giving corresponding decreases in conductivity. Moreover, during storage also the pH of the solutions increased from 6.5-7 to 8.3 giving a higher amount of ammonia and an increased risk for evaporation of ammonia.

Urine RO performance was analyzed in a pilot plant with a total membrane area of 0.9 m^2. The urine of Farm A and B was prefiltered through a flatbed filter with 30 µm openings, whereas the liquid of Farm C was filtered through a filter with 100 µm openings. Polyamide composite membranes used in the subsequent RO step had a retention of 99% for a 0.5% NaCl solution when operated at 15 °C and 40 bars. During urine filtration, the urine temperature was kept below 30 ºC (a compromise between high flux and NH_3 emissions) and the crossflow velocity was 2.4 m/s.

Figure 6 shows the permeability of the RO membranes during pilot operation using feeds from Farm A, B and C.

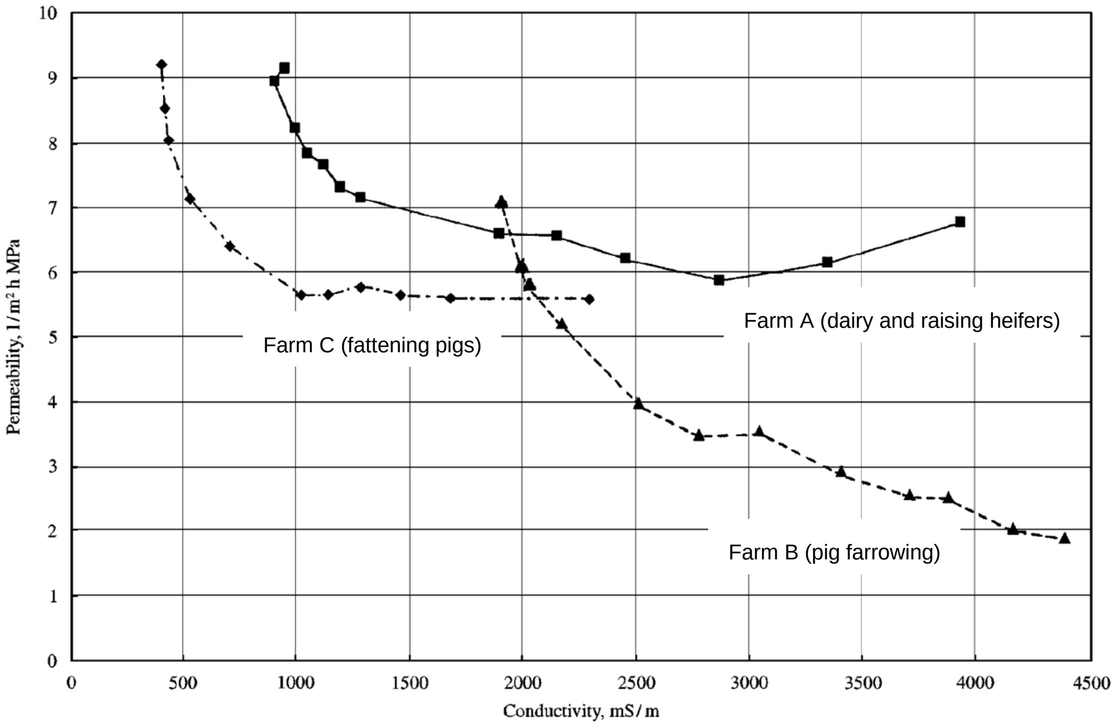

Figure 6: Temperature normalized permeability as a function of estimated conductivity for wastewater from farm A, B and C [11]. For comparison: fluxes obtained at reference Farm III (Manure) are in the order of 1-2 l/m^2 h bar.

The relatively high fluxes at the start followed by a strong decrease indicate considerable concentration polarization and severe fouling and deposition of organic material followed by the build-up of thick fouling layer increasing the resistance for permeation. Also, high amounts of small, low molecular weight substances are present that do not contribute to the conductivity of the solution but do increase the osmotic pressure of the solution and with that decrease the effective driving force for permeation (ΔP) over the membrane at a given applied pumping pressure.

Corresponding retentions for ammonia-nitrogen, nutrients (determined via COD - chemical oxygen demand), phosphorous and total solids are presented in figure 7.

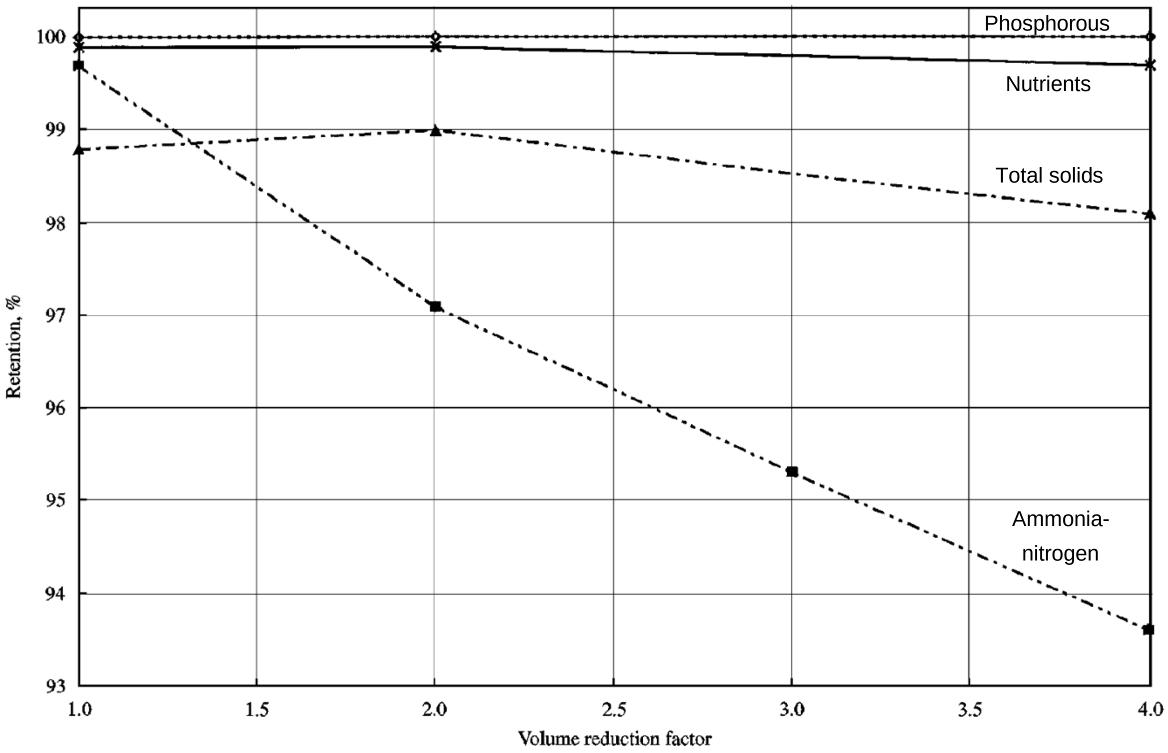

Figure 7: Retention of ammonia-nitrogen, nutrients (determined via COD - chemical oxygen demand), phosphorous and total solids [11].

The permeate quality in terms of ammonia-nitrogen and nutrients decreases with increasing feed concentration (volume reduction factor) whereas the phosphorous rejection is independent on the feed concentration showing a very high retention over the full concentration range.

Figure 8 subsequently shows the total nitrogen loss since collection of the urine and the nitrogen losses due to permeation. Clearly, the total loss in terms of ammonia (due to ammonia evaporation) is much higher than the loss due to permeation. However, a relatively large amount of nitrogen is lost due to permeation of urea to the permeate (product water) side of the RO, independent of the type of feed negatively impacting the product quality. Efforts to decrease the pH of the feeds to increase the retention for ammonia failed due to the good buffer capacity of the feeds and the authors recommend a fully covered system to prevent ammonia evaporation.

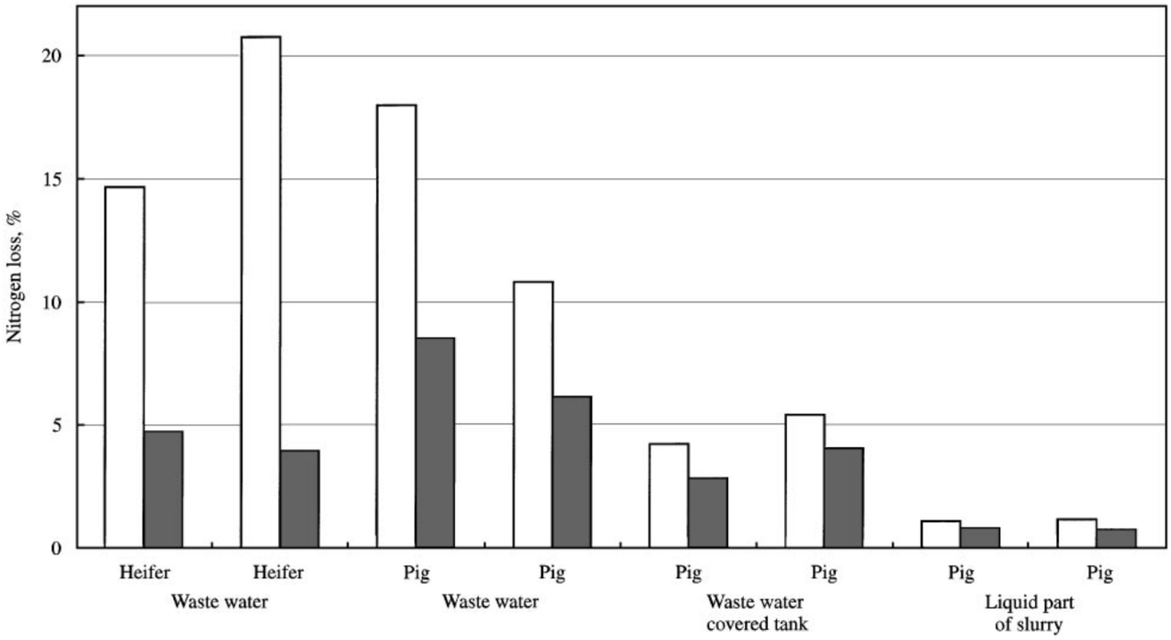

Figure 8: Total loss of nitrogen (white columns) and nitrogen loss to permeate (gray columns) for different feeds from Farm A, B and C [11].

3.4.2 Reverse osmosis treatment for human urine concentration

As literature on concentrating pig manure is scarce due to the associated challenges to collect urine only, also literature on the concentration and resource recovery of human manure is considered. Damtie et al. [12] very recently published an article about ammonia recovery from human urine as liquid fertilizer using hollow fiber membrane contactors. Hydrophobic porous membranes were used, and ammonia was evaporated through the membrane and captured in an acid solution on the permeate side of the membrane. A challenge of such a membrane contactor process is long term stable operation.

Patel et al. [13] published a review article about technologies for the recovery of nutrients, water, and energy from human urine. It was stated that urine if the best source for fertilizers as it contains 10-12 g/L nitrogen, 0.1-0.5 g/L phosphorous and 1.0-2.0 g/L potassium. Among the techniques used for recovery of nutrients various membrane techniques are discussed among others RO, nanofiltration (NF) and forward osmosis (FO; uses a draw solution with a very high salt concentration such that water is forced to permeate from the lower concentration urine to the high concentration draw solution). As a main conclusion Patel et al. indicate that forward osmosis is the best available technology for the water recovery and thus for concentrating the nutrients in urine, without or at minimal consumption of energy. However, experimental work in this technology is at its prior stage. In terms of RO, Patel et al. also indicate that very few studies on urine treatment using RO are available. Moreover, they mention that the major limitation of urine concentration with RO is the occurrence of fouling. A high solids or organics content in the feed solution induces severe fouling decreasing the water flux, requiring severe pretreatment and more regular chemical cleaning and with that increasing costs of operation while reducing membrane lifetime.

Following on this, Ek et al. [14] investigated the potential to use RO to concentrate nutrients from source separated urine. Urine was collected from Understenshöjden, a residential area with urine separating toilets. To simulate a BioP reject water, reject water from a sewage treatment plant with conventional precipitation with iron was used after addition of extra P. To prevent clogging of the membranes due to the presence of particles, three different pre-treatment technologies were evaluated: sieving through a 0.5 mm sieve, filtering with a 5 μm cartridge filter, and ultra-filtration (UF) with an UF membrane with a cut-off value of 100,000 Dalton. The effect of pre-treatment, pH (with different acids), pressure, and temperature on RO performance at pilot scale were studied. Two different membrane types were used: PCI AFC-99 and Filmtec SW30-HR.

Although there were differences in ultimate flux for the different pre-treatments (figure 9), these differences were small not justifying the higher costs for ultrafiltration pre-treatment. The researchers concluded that especially the removal of particles larger than 5-10 μm is essential and decided to select the 5 μm cartridge filter for further pre-treatment.

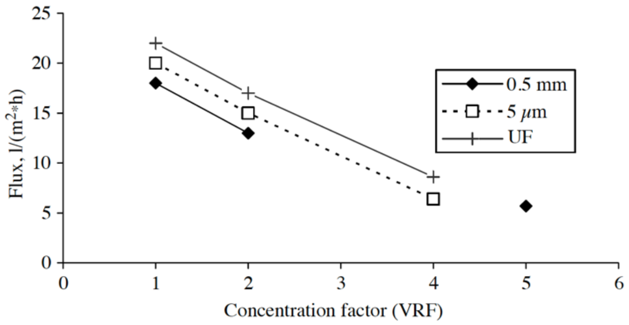

Figure 9: Flux as a function of the volume reduction factor (VRF) and type of pre-treatment for urine RO filtration [14].

The two membranes gave very similar results although the AFC had a slightly better separation of N, and about 20% higher flux, but the much lower price for SW or a similar spiral wound membrane makes this more economic. A transmembrane pressure of 5 MPa resulted in an almost 50% higher flux than at 4 MPa for urine at a VRF of 2. This justifies the more expensive equipment and higher pump energy used for 5 MPa operation.

The pH influenced both flux and retention. The influence on flux is probably due to the addition of extra salt to change the pH resulting in higher osmotic pressures of the solution and consequently lower driving forces for permeation. At operation at pH 7, the concentrate at a VRF of 5 contained 95% of the total N and 99.7% of the total P. The mean flux to reach a VRF of 5 was about 15 l/(m^2 h) at 30 ºC. Results for different pH values are summarized in table 4.

Table 4: Capacity and rejection performance for RO urine treatment at different pH values (5 mPa and 29 ºC) [14].

pH	Flux @VRF* 5 [L/m^2 h]	N in concentrate [%]	P (or K) in concentrate [%]
9.2	10.5	79	> 99.9
7.0	7.2	91	> 99.9
6.0	5.5	98	> 99.9

*VRF = volume reduction factor

The higher loss of N to the permeate at higher pH, is probably due to a higher membrane retention for of NH_4^+ than for NH_3. P and K were very effectively separated by both membranes. Ultimately, the optimum of pH for a specific RO process highly depends on the specific feed used and should be assessed for each situation individually based upon the amount of N recovered and the cost for RO to reach a certain VRF.

Finally, Ek et al. [14] compared RO using source separated urine and reject water from digestion of sludge in a sewage treatment plants with evaporation and precipitation of phosphorus and distillation of ammonia both in terms of recoveries (table 5) and costs (table 6). For RO pre-filtration with particle separation at 5–10 µm was sufficient to prevent clogging of the membranes. Separation of phosphorus (P), potassium (K) and sulphur (S) was almost 100%, while separation of nitrogen (N) was dependent on pH. The flux increased with temperature and pressure.

Table 5: Products recovered with different methods, % of total [14].

Method	N	P	K	VRF	Comments
Urine, RO	95	90	99	5	High salt, all impurities
Evaporation	95	100	99	20	Very high salt, all impurities
MAP + NH_3	3 + 85	90 + 0	0 + 0	125 + 10	Relatively pure
Reject, RO	90	92	97	20	High salt, all impurities
Evaporation	95	100	100	50	Very high salt, all impurities
MAP + NH_3	5 + 85	65 + 0	0 + 0	330 + 10	Relatively pure

*Although nitrogen recoveries reported in this table are very high, the actual value is highly dependent on the pH of the feed.

Table 6: Main resources used and estimated costs per m^3 treated media [14].

Method	Chemicals	Energy, kWh		Cost at 10 m^3/h, SEK		Total SEK at	
		Electr.	Heat	Capital	Operation	10 m^3/h	2 m^3/h
Urine, RO	6 kg H_2SO_4	8	4	6.6	16	23	32
Evaporation	13 kg H_2SO_4	30	0	20	28	48	78
MAP + NH_3	0.6 kg MgO	0.6	66	1.9 + 3.8	2.7 + 14	22	42
Reject, RO	2.9 kg H_2SO_4	5	0	4.5	8.7	13	21
Evaporation	4.2 kg H_2SO_4	30	0	20	19	39	69
MAP + NH_3	0.14 kg MgO	0.9	26	2.1 + 3.8	1.5 + 6.0	13	32

Although the calculations of costs are relatively rough, the authors concluded that of the methods investigated, RO gives the lowest cost. Costs might be competitive for urine treatment due to the high amounts of nutrients that could be recovered under these circumstances. However, in the case of reject water these values are not competitive due to the lower recoveries. Authors report that the most expensive is the separation of urine from the rest of the sewage. This also drastically decreases the load of N and P. Source separated urine significantly helps to improve this.

4. Materials and Methods

4.1 Materials

Four different liquid manure fractions were provided by Nico Verdoes (WUR).

I. Pure urine from fattening pigs
II. Contaminated urine originating from a conveyer belt
III. Thin manure after mechanical separation, feed RO
IV. Thin digestate after monodigester and separator

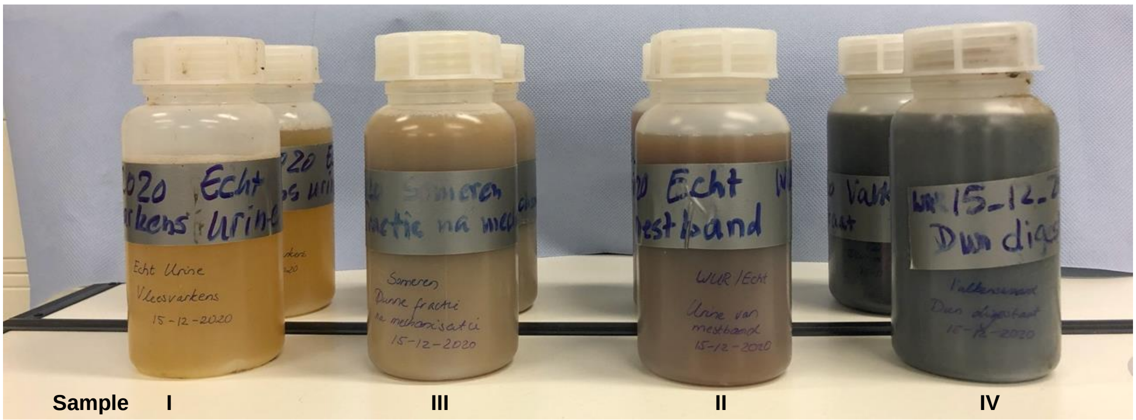

Figure 10: Samples I to IV directly after receiving.

Via Nico Verdoes we received, based on literature research and the expertise of the Livestock Research department, the estimated compositions of the different fractions as reported in table 7. For completion, we added the digestate data as supplied one of the partners.

Table 7: The composition of the different mineral streams as supplied by Nico Verdoes. * The digestate data are supplied from a digester that is operated by one of the partners.

Component	Amount	Pure urine	Contaminated urine	Thin manure	Thin digestate*
Dry matter	[g/kg]	24	28	17	11
pH	-	8	9	8	8
Conductivity	[mS/cm]	-	41	28	31
N-Total	[g/kg]	7	6	3.4	3.3
$N-NH_4$	**[g/kg]**	**0.2**	**5**	**2.6**	**2.6**
Ureum	**[g/kg]**	**5.5**	**-**	**-**	**-**
K	[g/kg]	3.6	5	3.1	3.2
Ca	[g/kg]	0.2		0.1	0.1
Mg	[g/kg]	0.2		0.1	0.1
Na	[g/kg]	-	0.8	0.7	0.9
HCO_3	[g/kg]	0.2	-		11
SO_4	[g/kg]	-	1.7	0.1	0.1
Cl	[g/kg]	-	2.8		1.9

After receiving the samples, the photo presented in figure 12 was taken, after which the samples were kept in a fridge at 4 °C for storage until further use.

4.2 Methods

4.2.1 Conductivity and pH

From all the samples the conductivity was determined using a Greisinger GMH3400 conductivity meter and the pH was measured using a WTW Inolab pH730 device.

4.2.2 Silt Density Index (SDI) measurement

To evaluate the filterability of the four different feeds, silt density index (SDI) measurements were performed (figure 11). The SDI is a standardized ASTM method to evaluate the colloidal and particle fouling potential of a specific feed in comparison to other feed. All samples obtained were thus subjected to SDI testing. For sample I and III this was done with the feed as received. However, as all samples contained a lot of particulate material, next, before determining the SDI value of all samples, two prefiltrations were carried out. First the samples were filtered through paper filter from Farm III. This paper had pore sizes in the range of 100 μm. Next, the obtained paper filtered solutions were filtered using a Bekipor 5AL3 metal filter (Bekaert S.A., Zwevegem Belgium). This filter had an effective filter area of 15 cm^2, a pore size of 5 μm, a thickness of 0.37 mm and a porosity of 80%. The SDI of all 5 μm filtered samples was subsequently determined.

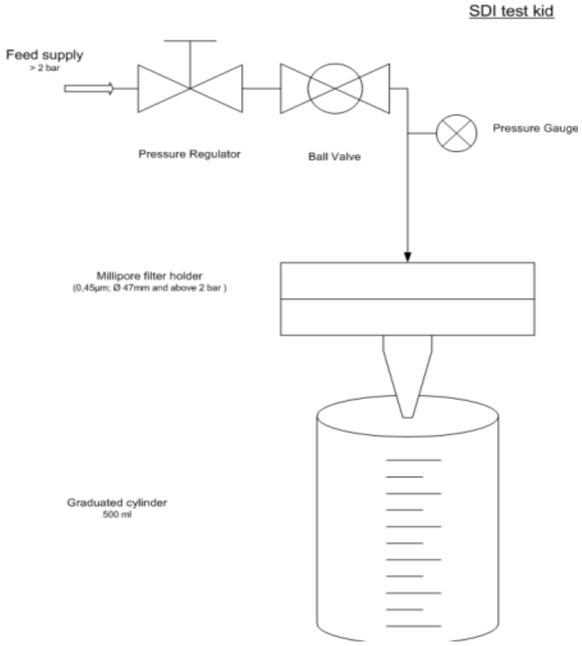

Figure 11: Schematic of SDI setup.

Membrane fouling is the main cause of permeate flux decline and loss of product quality in reverse osmosis (RO) systems, so fouling control dominates RO system design and operation. Sources of fouling can be divided into four principal categories: silt (particular), scale, bacteria (bio fouling, growth of bacteria) and organic fouling (oil, grease).

Fouling control involves pre-treatment of the feed water to minimize fouling as well as regular cleaning to handle fouling that still occurs. Fouling by particulates (silt), bacteria and organics generally affects the first modules in the plant the most. Scaling is worse with more concentrated feed solutions, therefore the last modules in the plant are most affected, because they are exposed to the most concentrated feed water.

The Silt Density Index (SDI) is a widely accepted method for estimating the rate at which colloidal and particle fouling will occur in water purification systems, especially using RO or nanofiltration membranes. SDI is a measurement of the fouling potential of suspended solids. It's not measuring the quantity of particular matter, since the size, shape vary. The SDI test is used to predict and then prevent the particulate fouling on the membrane surface. The test is defined in ASTM Standard D4189, the American Standard for Testing Material.

It measures the time required to filter a fixed volume of water through a standard 0.45µm pore size microfiltration membrane with a constant given pressure of 30 psi (2,07 bar). The relative difference between the initial time to collect that fixed volume of water (500 ml) and the time of a second measurement after normally 15 minutes (after silt-built up) to collect that same amount of fixed volume represents the SDI value and characterizes the colloidal and particulate fouling behavior of the feed solution.

To calculate the SDI, the following equation can be used:

$$SDI = 100 \cdot \frac{(1 - \frac{t_i}{t_f})}{t_t} \qquad (6)$$

Subsequently, the plugging factor can be calculated (equation 7) and that defines the fraction of the pores covered by foulants from the feed after the elapsed measurement time:

$$PF = \frac{SDI_{15}}{6.7} \cdot 100\% \qquad (7)$$

Where:
SDI = Silt density index
SDI_{15} = Silt density index based on 15 minutes measurement
t_t = Total test time (usually 15 minutes, but less if 75% plugging occurs in < 15 minutes)
t_i = Initial time in seconds required to obtain sample.
t_f = Time required to obtain sample after 15 minutes (or less)
PF = Plugging factor (%)

Table 8 provides the translation of the measured SDI values to RO membrane operation performance. Important to realize is that the values only relate to colloidal, particulate fouling and do not provide information on other foulants or fouling in general. Moreover, in the ASTM method, measurement time is 15 minutes and in that 15 minutes at least two times 500 ml of permeate is collected. If permeate fluxes are low, collection of 100 ml sample volume may be considered for reliable SDI values.

Table 8: Translation of the SDI values to consequences for RO filtration performance.

SDI value	**Fouling in RO operation**
SDI < 1	Several years without colloidal fouling
1 < SDI < 3	Several months between cleaning
3 < SDI < 5	Particular fouling likely a problem, frequent cleaning
SDI > 5	Unacceptable fouling. Additional pre-treatment is needed

Notes:

1 Time to collect 500 ml should be approximately 5 times greater than the time to collect 100 ml. If 500 ml collection time is much greater than 5X, the SDI should be calculated using 100 ml collection times.

2 For accurate SDI measurements, PF should not exceed 75%.

5. Results and discussion

5.1 Composition of the supplied samples

Four different samples as listed in table 9 were collected by the WUR (on behalf of Nico Verdoes) and split in two parts. One part was supplied to the TU/e while the other part was taken to the WUR for analysis. After receiving the samples photos were taken as depicted in Figure 10. Then the samples were stored in a refrigerator at 4 °C till they were analyzed. The WUR samples were stored in a freezer -80 °C up to the moment that the composition of the different samples was determined.

Table 9: Obtained urine and manure samples for SDI analysis.

No.	**Name**	**Description**
I	Urine	Pure urine from fattening pigs
II	Contaminated urine	Contaminated urine originating from a conveyer belt
III	Thin manure	Thin manure after mechanical separation, feed RO
IV	Thin digestate	Thin digestate after monodigester and separator -

Table 10: Composition of the supplied samples, analyzed by the WUR. The most important numbers are highlighted. The red highlight is most likely too low.

	totaal-N	ammonium-N	Natrium	Kalium	pH	EC	Ureum-N	Chloride	Sulfaat	Calcium	Magnesium	droge stof	CO2	Si	Si	Si
	WI 4.25-115	WI 4.25-103	WI 4.25-122	WI 4.25-122	WI 4.25-113	WI 4.25-113	WI 4.25-121	IC	IC	ICP	ICP	WI 4.25-111		meting 1e	2e	
	g/kg	g/kg	g/kg	g/kg		mS/cm	g/l	g/l	g/l	g/kg	g/kg	g/kg	g/l	mg/kg	mg/kg	gem.
1 - zuivere urine	3.08	0.23	0.90	2.70	7.9	12.4	2.27	1.37	1.18	0.15	0.10	19.7	4.10	22	23	22
2 - onzuivere urine	6.17	4.87	0.80	4.50	9.4	39.0	0	2.52	2.55	0.20	0.28	26.5	8.30	35	34	34
3 - dunne fractie	1.88	1.81	0.68	2.74	8.2	22.7	0	1.38	2.40	0.05	0.11	10.0	6.60	3.4	16	9.4
4 - dunne digestaat	5.56	4.15	1.08	3.15	8.2	33.3	0	1.78	0.19	1.33	1.00	41.1	13.10	506	527	516

Silica is highlighted because this element is very decisive in the membrane scaling. Especially when the organic fouling is low and at high pH's (e.g. > 8.5) a fine dense highly impermeable silica oligomer layer will be formed on the membrane surface that is difficult to remove and is responsible for severe flux decline that often results in early membrane replacement [15].

5.2 Osmotic pressure

Based on the data presented in table 10 the osmotic pressure is calculated for the first 3 samples. The osmotic pressure calculation is based on the ammonium-N where the molar urea-N concentration is divided by two since one molecule urea contains two nitrogen atoms.
The osmotic pressure from the “zuivere urine” was 7 bars which was comparable to the osmotic pressure from the “dunne fractie”, 10 bars. The osmotic pressure of the “onzuivere urine” was with 18 bars significantly higher. This is mainly contributed to the conversion of urea into two ammonium ions which doubles the contribution to the osmotic pressure. Next to this based on table 2 the amount of potassium and that of the anions chloride and sulfate and bicarbonate are significantly higher than in the “zuivere urine”. Therefore the maximum concentration factor that can be achieved when applying the same hydrostatic pressure is about factor two lower. However considering that the initial ionic concentration is also a factor 2 higher it will result in a mineral concentrate with the same strength. We estimate that a (light) pretreatment is preferred, to lower the risk of membrane fouling or module clogging by particulates that are present in the “onzuivere urine” before starting the concentration process.

5.3 Visual observations

After receiving, the samples were stored in a fridge at 4 °C. From each batch 80 ml fractions were taken and stored in a transparent glass bottle in order to allow a better optical inspection. Figure 12 clearly demonstrates that all samples contained solid material that was sensitive to gravitational forces.

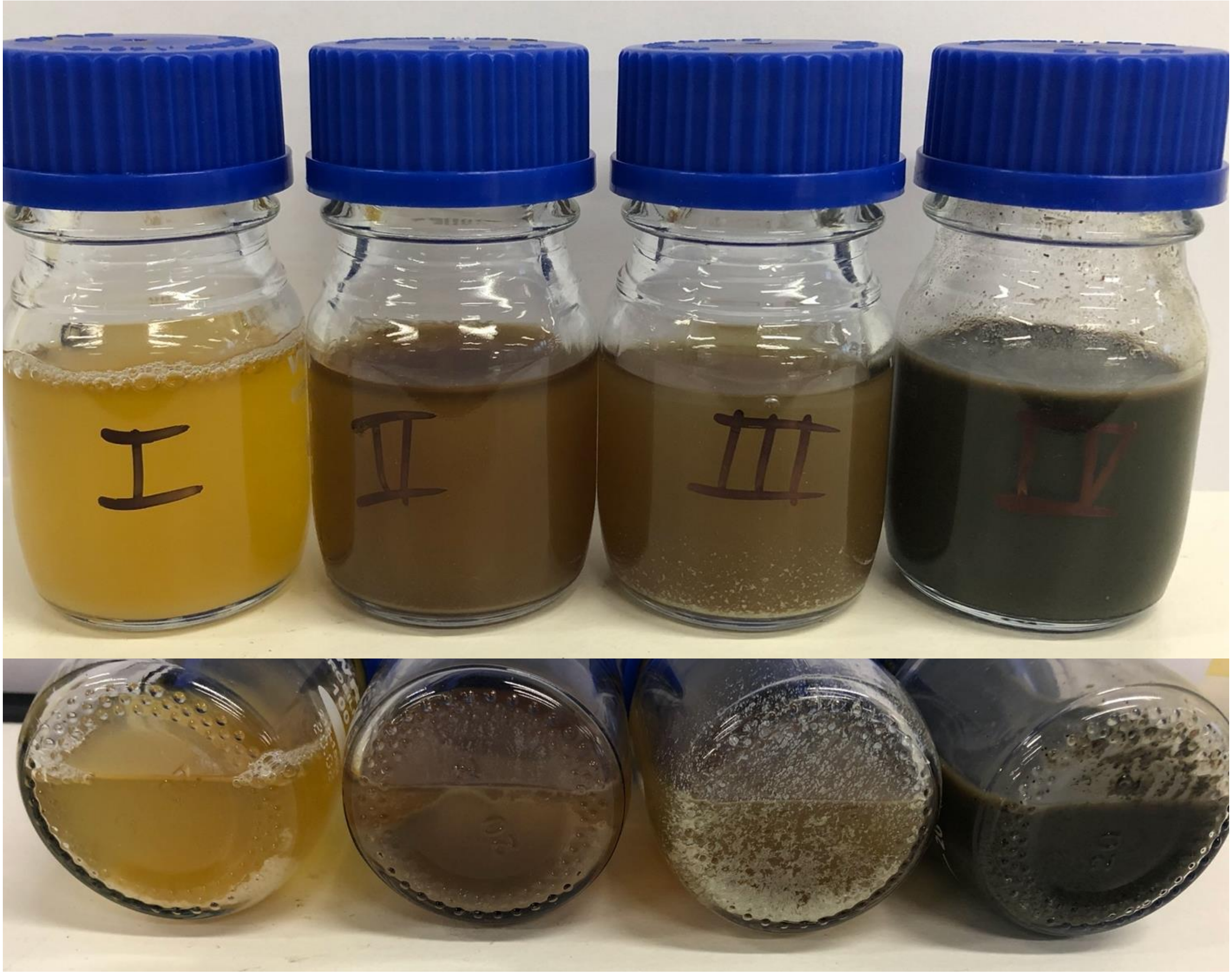

Figure 12: Sedimentation by gravity in 80 ml samples, sample identifier I to IV from left to right (201221).

This was even more clear after centrifugation of the samples (figure 13). Even the pure urine sample contained relatively large amount of solid material still (figure 14).

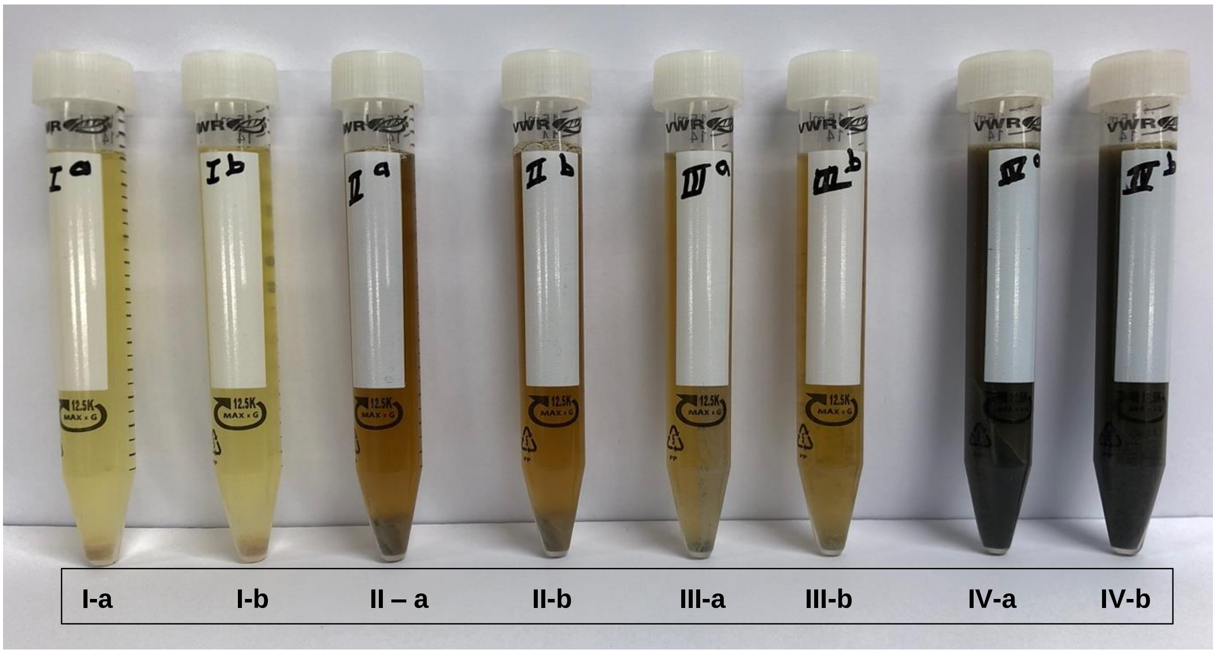

Figure 13: Separation between solid and liquid phase after centrifugation (3 minutes @ 6500 rpm) for all obtained samples.

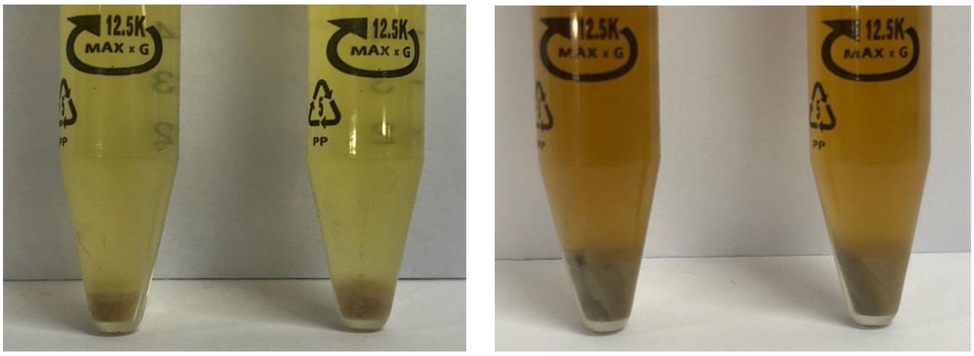

Figure 14: Separation between solid and liquid phase after centrifugation (3 minutes @ 6500 rpm) for left: pure urine (I) and right: contaminated urine (II).

5.4 Conductivity and pH

From all the samples the conductivity and pH were measured. The conductivity is directly related to the concentration of charged species. The osmotic pressure of the solution is directly related to the total number of all (not only charged) species in solution. Assuming that only charged species are present in the solutions, the measured conductivities can be related to the osmotic pressure. Based on our experience with manure slurry in most of the industrial processes the maximum operational pressure is 40-60 bar which coincides with a conductivity of about 50 mS/cm. For the streams listed in table 9 this implies a maximum concentration factor in RO that can be obtained ranging between 1.5 - 2.5.

Table 11: Conductivities and pH values of the four untreated samples.

Sample	Identifier	mS	pH
I	Urine (direct from pigs Echt)	20.6 (12.4)	7.50 (7.9)
II	Polluted urine (conveyer belt, Echt	39.1 (39.0)	5.75 (9.4)
III	Manure slurry (before RO Verhees, Someren)	21.9 (22.7)	7.29 (8.2)
IV	Digestate (after monodigester, Valkenswaard)	26.6 (33.3)	5.19 (8.2)

Conductivity and pH measured after 4 days in freeze at 4 ^{o}C (TU/e)

Between brackets measured after one month storage in -80 ^{o}C (WUR)

5.5 SDI

5.5.1 Introduction

The SDI values of the native samples (I and III) were determined. However, as all native samples contained relatively high amounts of larger solid material, apart from measuring the filtration behavior of untreated samples, we also applied a filtration using filter paper (Farm III; approx. 100 μm followed by a prefiltration with a 5 μm metal filter as we estimate that this is a minimum requirement in the real application.

Still, because of the severe fouling, even after pre-filtration, the samples could not be treated according to the ASTM protocol for SDI measurements. For this reason we adjusted the protocol such that based on smaller permeate volumes we were able to calculate an SDI value. To eliminate the startup inaccuracy t_i was taken from 10 to 20 seconds. For t_f the time interval was taken after 15 minutes that was necessary to collect the same permeate volume as was collected in t_i. Important is to realize that the real SDI values are significantly higher than those reported here do to adjustment of the measurement protocol to volumes 10-100 times smaller than the ASTM method. This means that the outcome of the SDI measurement gives a too optimistic estimation from the RO-filtration performance. In the next paragraphs, the experimental observations, and the corresponding sample SDI values of the four different samples are discussed.

5.5.2 Sample IV: Thin digestate

The obtained sample was obtained from a digester. Fresh manure is fed to a grinder to cut the larger substances into smaller sizes. Subsequently, this stream is fed to a mono-digester (plug flow) with an average residence time of 12 days. Finally, the remaining digestate is fed to a screw separator where to separate the solids for the liquid fraction. The remaining thin digestate is used to fertilize the land. This stream is also delivered for analysis at the TU/e (stream IV). In normal operation, this

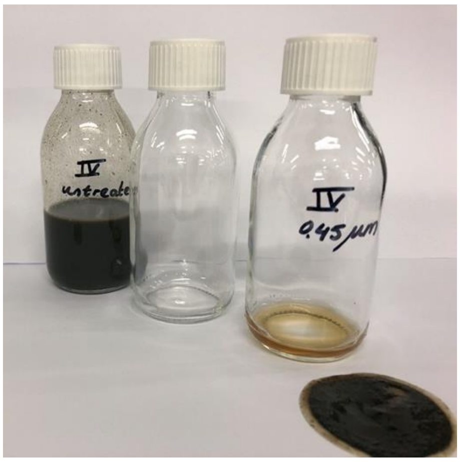

Figure 15: Fraction VI: Thin digestate: untreated and 0.45 μm SDI permeate and the fouling layer on the membrane used for SDI determination.

Figure 16: Sample IV digestate: due to the highly viscous, high solids solution, severe fouling occurred and only a few ml of permeate could be collected. Image shows precipitation of 25 ml filtrate on a type 2 paper band filter Farm III).

liquid fraction is without further treatment directly used for fertilization of own land and neighboring meadows. For the future, membrane distillation is under evaluation but that resulted in nitrogen breakthrough to the permeate site which also makes the addition of an additional RO step necessary to prevent nitrogen leakage with the discharge water.
As a consequence of the above treatment, the supplied liquid is highly viscous and has a high solid and suspended particles content (figure 15). Because of the high amounts of suspended solids in the digestate, direct filtration of the untreated sample to determine its SDI was not possible (SDI value fully out of specifications). For this reason, we tried a prefiltration with type 2 paper filter (as is used in the manure slurry process (Farm III)) but even at an area of 78 cm^2 and an applied pressure of 5 bar, only a few ml of permeate was produced. Figure 16 shows the fouling layer present on the paper filter after only a few ml of permeation. Since the permeate flux of the pretreatment was below 0.1 g/minute, it was impossible to collect sufficient pre-filtrated permeate to determine the SDI. Consequently, only the SDI of native thin digestate was determined.

The untreated thin manure has an SDI value of 6.56 and a plugging factor of 89%. This is close to the maximum SDI value that can be obtained, and the very high plugging factor clearly illustrate almost complete pore blocking of the filter, clearly confirming that thin digestate (IV) cannot be fed to the RO. For completeness the SDI filtration curve is given in figure 17.

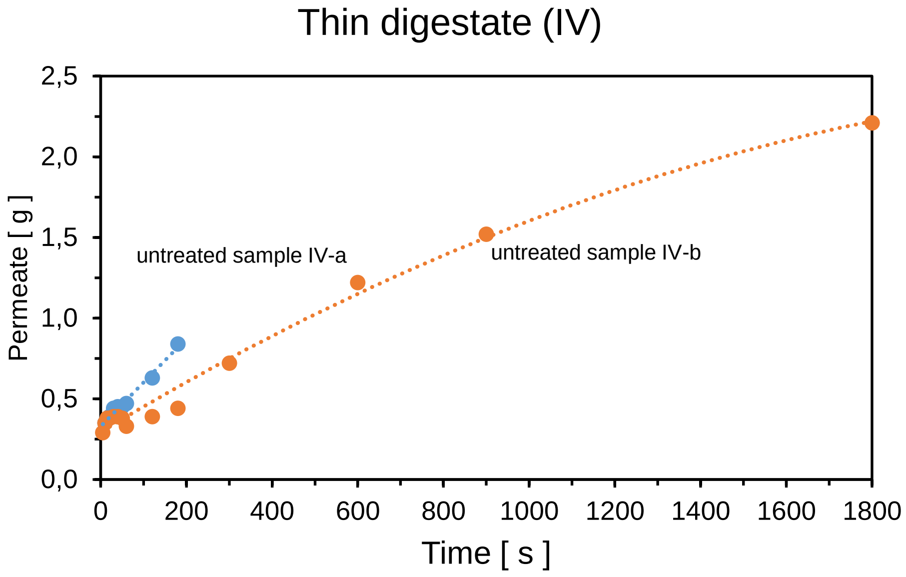

Figure 17: SDI filtration curves of thin digestate (IV).

5.5.3 Sample III: Thin manure

Sample III is obtained from Farm III and is taken just before the RO system. In this system the liquid fraction has had an extended pretreatment: Flocculation with polymer and Fe_2Cl_3; belt press; 2nd polymer flocculation; DAF and paper filter. The untreated sample showed some white solids that might originate from the flocculants (figure 12).

The untreated thin manure has an SDI value of 5.84 and a plugging factor of 84%. After the 100 μm paper band and 5 μm prefiltration the permeate flux was two times higher but the SDI value increased to 6.52 with a plugging factor of 97%. This is most likely due to instability of the thin manure in time and because due to the prefiltration the particles in the fouling layer are smaller making the layer more compact. For completeness the SDI filtration curve is given in figure 19.

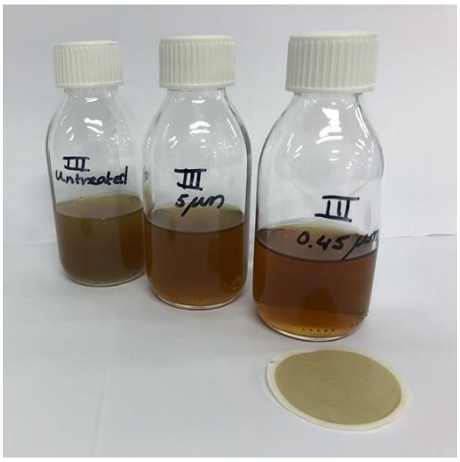

Figure 18: Fraction III: Thin manure: untreated, 0.5 μm prefiltered and 0.45 μm SDI permeate and the fouling layer on the membrane used for SDI determination.

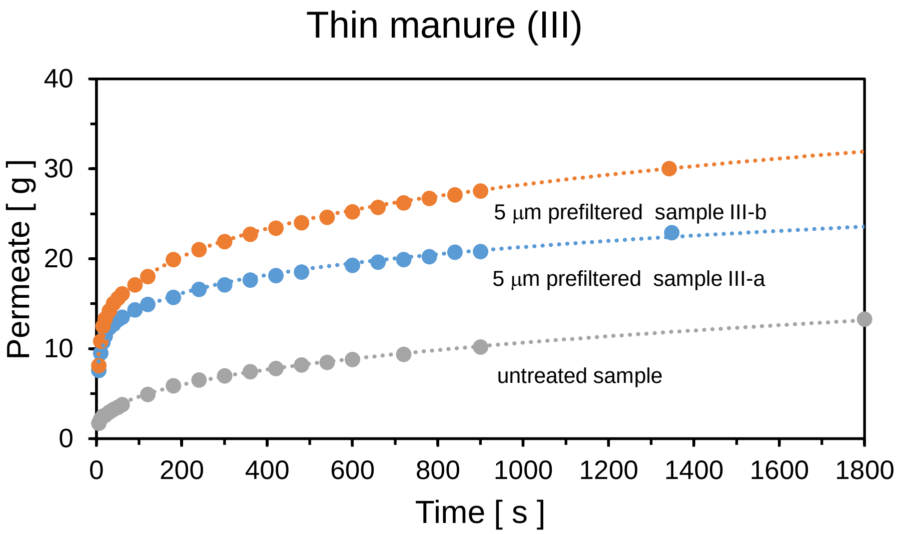

Figure 19: SDI filtration curves of thin manure (III).

5.5.4 Sample II: Contaminated urine

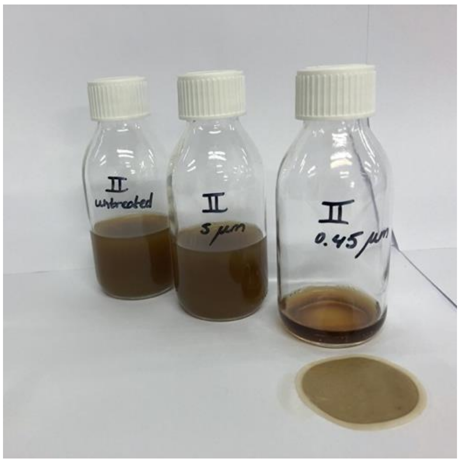

Figure 20: Fraction II: Contaminated urine: untreated, 0.5 μm prefiltered and 0.45 μm SDI permeate and the fouling layer on the membrane used for SDI determination.

Sample II is the liquid fraction that is collected in the pig house under the conveyer belt. For this reason, the urine is polluted with feces and materials from the piggery. The color of this sample (figure 20) is much darker than that of the “clean” urine (sample I) and contains more solid see also the centrifugal tubes in figures 13 and 14.

After the 100 μm paper band and 5 μm prefiltration and SDI value of 6.14 and 4.29 with corresponding plugging factors of 92 and 64%. The second value may suggest that this stream is easier to use in RO, however, due to the very high degree of fouling, the SDI is very sensitive to small changes in the initial phase of the measurement. The SDI values well above 4 clearly confirm that also this stream needs significant pretreatment before usage in RO. For completeness the SDI filtration curve is given in figure 21.

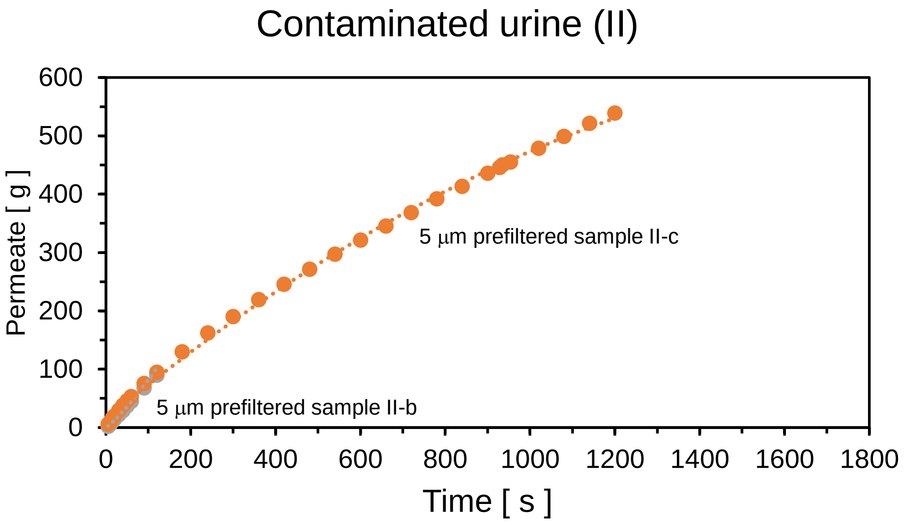

Figure 21: SDI filtration curve of contaminated urine (II).

5.5.5 Sample I: Clean Urine

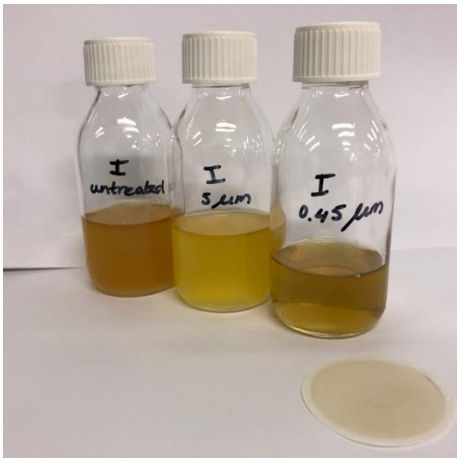

Figure 22: Fraction I: Pure urine: untreated, 0.5 µm prefiltered and 0.45 µm SDI permeate and the fouling layer on the membrane used for SDI determination.

Sample I is pure urine directly collected from the pig. Therefore this sample should be very clean. Surprisingly, also this sample clearly shows precipitates (figure 13 and 14). Also the sample is brighter in color. However, after a few days of colors the amount of solid material in the solution severely increased, suggesting that the sample has a very low stability in time, even though it was stored at a temperature of 4 °C.

For the untreated pure urine the SDI value was determined twice 20 hours after receipt of the samples and values of 3.51 and 3.76 with plugging factors of 52 and 56 % were obtained. Five days later, the samples were pre-filtered with paper band and a 5 µm metal filter and the SDI was determined again. This time, SDI values of 2.47 and 5.89 with corresponding plugging factors of 37 and 89 % were obtained. The high discrepancy between the two obtained SDI values confirms the high instability of the feed as also observed by the naked eye. The high value of 5.89 is due to the increased loading of solid material as observed by the naked eye, despite the pre-filtration due to instability of urine in time. Moreover, due to the prefiltration especially the smaller particles remain, forming a denser, more compact fouling layer. For completeness the SDI filtration curve is given in figure 23.

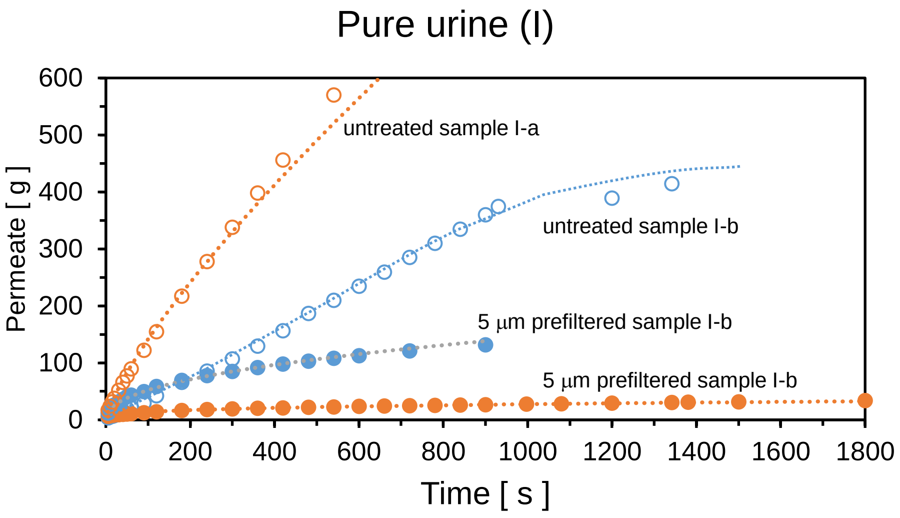

Figure 21: SDI filtration curve of pure urine (I).

To summarize the above results, table 12 lists the obtained SDI values for all samples.

Table 12: Experimentally determined SDI values and plugging factors for pure urine (I), contaminated urine (II), thin manure (III) and thin digestate (IV).

Sample	Urine	Contaminated urine	Thin manure	Thin digestate
Code	I	II	III	IV
Prefiltered (5 μm)	2.47 (37%)	6.14 (92%)	6.52 (97%)	6.56 (98%)
	5.98 (89%)	4.29 (69%)	6.52 (97%)	n.a.
Untreated	3.51 (52%)		6.15 (92%)	
	3.76 (56%)			

SDI < 1 : Several years without colloidal fouling
1 < SDI < 3 : Several months between cleanings
3 < SDI < 5 : Particular fouling likely a problem, frequent cleaning
SDI > 5 : Unacceptable fouling. Additional pre-treatment is needed

6. Conclusions and recommendations

The major conclusions of the evaluation can be subdivided in the following aspects:

SDI and pretreatment
Even freshy delivered urine contained already some flocs and solid material resulting in an SDI value between 3 to 4. Although RO operation is possible in such cases, these SDI values also clearly indicate that particulate fouling is likely to be a problem and regular cleaning is necessary. Due to the very limited stability of urine in time, this is even more severe in cases where collected urine is not immediately used in the RO. In such cases increased flocculation and sedimentation of solid material increases the amount of solid material in the feed resulting in increased fouling and an expected strong decrease in flux as well. As a consequence, also pure urine will need pre-treatment to remove larger particles and flocs. However, this may also impact the nature of the fouling layer as smaller particles may form a denser, more compact cake layer.

Concentration factor
The concentration factor of the mineral concentrate that can be reached depends on the effective transmembrane pressure which is the difference between the hydrostatic pumping pressure and the osmotic pressure of the mineral (liquid manure) stream. The osmotic pressure of a solution is related to the amount of particles and ions present in the solution and is therefore related to the conductivity of the solution. In most manure treatment plants the applied pumping pressure is approx. 40 bar in the first RO stage, which results in a concentrated stream with a conductivity of 50 mS (concentration factor 2 - 3). Since the conductivity of pure urine is only a little lower of that of thin manure it is estimated that also the maximum concentration factor for “zuivere urine” is 2 - 4.

Scaling
Literature extensively reports the occurrence of calcium, magnesium, and silica scaling in RO applications. Especially at high concentration factors, local concentrations of these components close to the membrane surface can reach very high values close to or even above the solubility product values of the respective components. From our previous study with pretreated manure RO filtration, especially serious silica scaling resulting in severe flux decreases was regularly observed in several industrial installations. The analysis of the WUR showed that the Si content in “zuivere urine” and “onzuivere urine” is comparable with that in thin manure which means that also here at higher pH values there is a severe risk of formation of dense impermeable silica oligomers on the membrane surface.

Stability of the feed
During the experiments performed, it was clearly observed that especially the urine samples were not stable in time. With increasing time, the turbidity of these samples increased every day although the samples were stored in a fridge at 4 °C. Flocculation and the deposition of solid materials seemed to occur resulting in higher membrane fouling tendency of the feed. Therefore, it is highly recommended to treat urine directly after collection.

Flux values
The flux values that can be obtained in practice are very hard to predict based on the only very few literature data reported on urine filtration. The very few studies on this topic present values in the order of 2-6 l/m^2 h 10 bar (= 0.2 - 0.6 l/m^2 h bar). Researcher however also report severe evaporation of ammonium and co-permeation of urea compromising the product water quality. For comparison, the RO installation at Farm III (manure treatment) produces fluxes in the range of about 9 l/m^2 h 40 bar (= 0.1-0.2 l/m^2 h bar). Overall, actual fluxes that can be obtained in a specific situation are highly

dependent on e.g. the supplied feed quality, the applied pre-treatment, used additives and applied conditions.

NH_3 emission and urea losses to the permeate fraction.
Urea is converted in ammonium (NH_4^+) by the enzyme urease which is present in the feces. When the feces and urine are collected separately no NH_4^+ will be formed. In liquid manure NH_4^+ is in equilibrium with ammonia (NH_3). The pKa of ammonium is 9.2 this means that at a pH of 9.2 the ratio NH_4^+ NH_3 is 1. At lower pH values the equilibrium is in favor of the NH_4^+. During the concentration in the RO process the NH_3 permeates the membrane. As a consequence, NH_4^+ is converted to NH_3 in order to re-establish the equilibrium. Therefore, operation at lower pH is beneficial to lower the NH_3 exhaust from the system (and storage). However, a newly emerged major disadvantage of separate collection of feces and urine is that now the nitrogen is present as urea which retention by RO membranes is very limited and will therefore end up in the discharged water requiring an additional post treatment to fulfill the environmental discharged regulations.

7. Bibliography

[1] G. Holm, "Heathline," 26 July 2017. [Online]. Available: https://www.healthline.com/health/osmolality-urine#results. [Accessed 25 11 2020].

[2] M. Mulder, Basic principles of membrane science (second edition), Dordrecht: Kluwer Academic Publishers, 1996.

[3] W. Shaw and J. Bordeaux, "The decomposition of urea in aqueous media," *J. Am. Chem. Soc.,* vol. 77, no. 18, pp. 4729-4733, 1955.

[4] A. Zarebska, D. R. Nieto, K. V. Christensen, L. F. Søtoft and B. Norddahl, "Ammonium Fertilizers Production from Manure: A Critical Review," *Critical Reviews in Environmental Science and Technology,* vol. 45, pp. 1469-1521, 2015.

[5] T. T. Canh, M. W. Verstegen, A. J. Aarnink and J. W. Schrama, "Influence of dietary factors on nitrogen partitioning and composition of urine and feces of fattening pigs," *J Anim Sci,* vol. 75, pp. 700-706, 1997.

[6] L. Massé, D. I. Masse and Y. Pellerin, "The effect of pH on the separation of manure nutrients with reverse osmosis membranes,," *Journal of Membrane Science,* vol. 325, p. 914, 2008.

[7] S. Lee and R. M. Lueptow, "Reverse osmosis filtration for space mission wastewater: membrane properties and operating conditions," *Journal of Membrane Science,* vol. 182, pp. 77-90, 2001.

[8] S. Lee and R. M. Lueptow, "Membrane Rejection of Nitrogen Compounds," *Environ. Sci. Technol.,* vol. 35, pp. 3008-3018, 2001.

[9] H. Willers, R. Melse and N. Ogink, "Concentration of urine from fatteners combined with ammonia removal by scrubbing exhaust air of a pig house," in *Proceedings of the Ninth International Symposium on Animal, Agricultural and Food Processing Wastes* , Durham, North Carolina (NC), USA, October 12-15, 2003.

[10] M. Mondor, L. Masse, D. Ippersiel, F. Lamarche and D. Masse, "Use of electrodialysis and reverse osmosis for the recovery and concentration of ammonia from swine manureUse of electrodialysis and reverse osmosis for the recovery and concentration of ammonia from swine manure," *Bioresource Technology,* vol. 99, pp. 7363-7368, 2008.

[11] L. Thörneby, K. Persson and G. Trågårdh, "Treatment of Liquid Effluents from Dairy Cattle and Pigs using Reverse Osmosis," *J. Agric. Engng Res.,* vol. 73, pp. 159-170, 1999.

[12] M. Damtie, F. Volpin, M. Yao, L. Tijing, R. Hailemariam, T. Bao, K.-D. Park, H. Shon and J.-S. Choi, "Ammonia recovery from human urine as liquid fertilizers in hollow fiber membrane contactor: Effects of permeate chemistry," *Environ. Eng. Res.,* vol. 26, no. 1, p. 190523, 2021.

[13] A. Patel, A. Mungray and A. Mungray, "Technologies for the recovery of nutrients, water and energy from human urine: A review," *Chemosphere,* vol. 259, no. 127372, 2020.

[14] M. Ek, R. Bergström, J. Bjurhem, B. Björlenius and D. Hellström, "The concentration of nutrients from urine and reject water from anaerobically digested sludge.," *Water Sci. Technol. 54,* vol. 54, no. 11-12, pp. 437-444, 2006.

[15] K.-G. Lu, M. Li and H. Huang, "Silica scaling of reverse osmosis membranes preconditioned by natural organic matter," *Science of the Total Environment,* vol. 746, p. 141178, 2020.

[16] G. Mason and D. Scott, "Renal excretion of potassium and potassium tolerance in the pig," *Quarterly Journal of Experimental Physiology,* vol. 57, pp. 393-403, 1972.

[17] M. Wafi, N. Hussain, O. El-Sharief Abdalla, M. Al-Far, N. Al-Hajaj and K. Alzonnikah, "Nano filtration as a cost-saving desalination process," *SN Appl. Sci.,* vol. 1(7), pp. 1-9, 2019.

[18] T. Jamil, I. Dijkstra and S. Sayed, "Usage of permeate water for treated domestic wastewater by direct capillary nanofiltration membrane in agriculture reuse," *Desalination and Water Treatment,* vol. 51, p. 2584, 2013.