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Mg²⁺- Based Fertilizer
Simultaneous Phosphorous and Nitrogen Recovery from Source-Separated Urine: A novel application for Fertiliser Drawn Forward Osmosis

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Abstract

Re-thinking our approach to dealing with wastes is one of the major challenges in achieving a more sustainable society. However, it could also generate numerous opportunities. Specifically, in the context of wastewater, nutrients, energy and water could be mined from it. Because of its exceptionally high nitrogen (N) and phosphorous (P) concentration, human urine is particularly suitable to be processed for fertiliser production. In the present study, forward osmosis (FO) was employed to mine the P and N from human urine. Two Mg\(^{2+}\)-fertilisers, i.e. MgSO\(_4\) and Mg(NO\(_3\))\(_2\) were selected as draw solution (DS) to dewater synthetic non-hydrolysed urine. In this process, the Mg\(^{2+}\) reverse salt flux (RSF) were used to recover P as struvite. Simultaneously, the urea was recovered in the DS as it is poorly rejected by the FO membrane. The results showed that, after 60% urine concentration, about 40% of the P and 50% of the N were recovered. XRD and SEM – EDX analysis confirmed that P was precipitated as mineral struvite. If successfully tested on real urine, this process could be applied to treat the urine collected in urban areas e.g., high-rise building. After the filtration, the solid struvite could be sold for inland applications whereas the diluted fertiliser used for direct fertigation of green walls, parks or for urban farming. Finally, reduction in the load of N, P to the downstream wastewater treatment plant would also ensure a more sustainable urban water cycle.

Keywords: Forward osmosis, Urine treatment, Phosphorous recovery, Nitrogen recovery, Fertilizer draw solution.
1. Introduction

Sustainability in wastewater treatment is one of the significant issues of this century (Xie et al. 2016). In particular, rethinking wastewater as a valuable resource is crucial in meeting adequate sanitation, water and fertilizer demand to feed a growing population (Elser and Bennett 2011, Xie et al. 2016). For these reasons, the efficient separation, treatment and reuse of human urine have gained increasing attention due to its inherent value potential (Maurer et al. 2006, Udert and Wächter 2012, Zhang et al. 2014). In fact, despite the low volumetric load of urine (i.e., less than 1% of the overall wastewater volume), it accounts for approximately 80% of the nitrogen (N), 50% of the phosphorus (P) and 55% of the potassium (K) load in most of the wastewater treatment plants (Liu et al. 2016, Maurer et al. 2006, Udert and Wächter 2012, Zhang et al. 2014). In particular, the amount of P contained in the urine is the single most significant source from urban areas (Zhang et al. 2014). Given the forecasted depletion of minable phosphorous rocks, reusing the P from waste streams could significantly enhance the sustainability of the urban water cycle (Xie et al. 2014, Xie et al. 2016).

Additionally, with the increase in the size and densities of modern cities high-rise buildings are already becoming necessary. In these, urine separation and gravity-driven collection might become a feasible choice. After treatment, the recovered nutrients could be reused in several urban applications such as green walls, parks or urban farming. Simultaneously, the load of N, P to the downstream wastewater treatment plants would be reduced, possibly making their operation less energy demanding (Ishii and Boyer 2015, Kavvada et al. 2017).

Despite the applicability of raw human urine for direct fertigation, its nutrients imbalance (i.e., mainly N), and low nutrients concentration (i.e., N: 0.9%, P: 0.06%, K: 0.3%) as well as possible contamination of unwanted xenobiotic (e.g. hormones and pharmaceuticals), makes
its large-scale application challenging. Besides, if transportation were required, then the costs of those above only, would offset the market value of urine as fertiliser (Maurer et al. 2006, Udert and Wächter 2012). Therefore, up-concentration of urine and/or selective nutrients recovery has recently attracted increased attention from the scientific community. Several technologies are currently studied to achieve these goals. Among them, nutrients precipitation as mineral fertiliser, or concentration as liquid fertiliser, have shown to be the most mature.

While recovering P, K as solid fertiliser is generally performed via struvite or K-struvite precipitation (Etter et al. 2011, Wilsenach et al. 2007), recovering N, P, K as liquid fertiliser has shown to be more challenging. Among the technologies investigated, nitrification-distillation (Udert and Wächter 2012), nanofiltration (NF) (Pronk et al. 2006), reverse osmosis (RO) (Maurer et al. 2006), adsorption (Tarpeh et al. 2017) and stripping (Tarpeh et al. 2018, Xu et al. 2017) were the most promising ones.

However, despite the high potential of the nitrification-distillation process, at present, its costly operation makes its applicability limited (Fumasoli et al. 2016). Pressure-driven NF/RO are not often employed due to their unsatisfactory rejection of urea and ammonia (the most predominant compounds in human urine) as well as high capital and operational costs (Maurer et al. 2006, Zhang et al. 2014). While conventional ammonia stripping is high energy and chemical intensive, electrochemical stripping in combination with electrodialysis and membrane stripping might be a more feasible approach (Tarpeh et al. 2018). However, the production of chlorination by-products (e.g., ClO$_3^-$, ClO$_4^-$) would still be a significant drawback of mediated electro-oxidation of urine (Zöllig et al. 2015). Finally, adsorption using ion exchange resins could be a useful technology to recover the N in the urine once the engineering questions about post-treatment of the eluent or eluate for pharmaceutical removal are addressed.
On the other hand, the process of P-recovery via struvite precipitation has been adequately addressed and understood, showing its cost-effectiveness, simple operation and safety in the final product (de Boer et al. 2018, Etter et al. 2011, Wilsenach et al. 2007, Xu et al. 2017). The downside of this process is that it does not alleviate the issue related to the large volume of human urine, and the recovery of both N and K is not addressed. Finally, this process also requires the addition of extra magnesium source to recover >90% of phosphorous, which comes at an additional cost (Maurer et al. 2006).

With these premises, to achieve the ambitious goal of combining urine volume reduction with nutrients recovery, while maintaining low operational costs, the feasibility of using osmotically driven forward osmosis (FO) process was recently investigated (Zhang et al. 2014). The principle of FO relies on the natural water transport across a semi-permeable membrane from a low concentration solution (feed) to a higher one (draw) until the thermodynamic equilibrium is reached (Phuntsho et al. 2012). The advantages of FO consist of lower fouling propensity as well as possible lower energy demand, especially when there is no need for draw solution regeneration or further feed brine management (Van Der Bruggen and Luis 2015). In particular, the concept of fertiliser driven forward osmosis (FDFO) has shown to be a viable FO application to reclaim and reuse wastewater and impaired waters for agriculture application (Chekli et al. 2017, Valladares Linares et al. 2016, Van Der Bruggen and Luis 2015). However, the primary inherent drawback of this process was identified as the reverse draw solute diffusion (RSF). In fact, the RSF of the fertiliser draw solution to the feed can compromise the final quality of the brine (i.e., by exceeding the nutrients concentration standards for direct brine discharge) but also can cause an economic loss of valuable fertiliser. Moreover, in the context of urine dewatering via FO, if RO brine is selected as DS, the loss in rejection of small and uncharged compound (e.g. urea) can contaminate the diluted
DS thereby jeopardising the process (Liu et al. 2016, Zhang et al. 2014). Zhang et al. (Zhang et al. 2014) have already tried to apply FO to concentrate human urine, using RO brine as DS. Their study showed that urea is practically not rejected by the FO membrane, therefore, impeding a safe discharge of the diluted RO brine in the environment.

We herewith present a novel FDFO concept for concentrating human urine, where both limitations of FO (i.e., RSF of the draw solutes and urea/NH₃ rejection loss), are beneficial to recover both nitrogen and phosphorous from urine. In fact, in this study, the feasibility of using a Mg²⁺-based fertiliser draw solution to dewater fresh (i.e. non-hydrolysed) human urine is investigated. In this concept, the reverse solute diffusion will trigger P-recovery via struvite precipitation, while the rejection loss of urea/NH₃ will enrich the Mg-fertiliser with valuable nutrients. At the same time, the final volume of urine will be reduced thereby improving the efficiency in downstream processes for N-recovery (e.g. ammonia stripping).

This initial study will address the following: (1) Screening of suitable Mg²⁺-fertiliser draw solutions based on FO performance, (2) Comparison between experimental results and model-based predictions and, finally, (3) Critical analysis of the process efficiency and feasibility regarding nutrients/water recovery and waste volume reduction.
2. Materials and Methods

2.1 Feed and draw solution

Figure 1 Schematic diagram of the process.

In Figure 1 the schematic representation of the system is displayed for a better understanding of the process. The synthetic fresh urine feed solution (FS) was prepared according to the recipe of Udert et al. (Udert et al. 2006), and its composition is displayed in
Table 1. Fresh urine was selected over stored urine because of several reasons. Firstly, fresh urine has about half the osmotic pressure compared to hydrolysed urine. This means that, theoretically, higher $J_w$ and concentration can be achieved when fresh urine is chosen. Secondly, the acidic pH of fresh urine (i.e. 5.5 - 6.5), caused by the presence of uric and oxalic acids, would likely reduce membrane scaling during the operation. Nevertheless, real urine is a very dynamic solution in which urea, if stored in non-sterile conditions, is hydrolysed to NH$_3$/NH$_4^+$ and carbonate. The urea hydrolysis process causes a rise in the pH to around 9 triggering the precipitation of Mg$^{2+}$ and Ca$^{2+}$ in the form of carbonates and phosphates (Maurer et al. 2006, Randall et al. 2016). Therefore, the experiments conducted in this study aim at validating the initial hypothesis but further investigations using real urine should be performed. MgSO$_4$ and Mg(NO$_3$)$_2$ were finally selected as suitable Mg-fertiliser DS for this application. In fact, to our knowledge, the only other soluble Mg-fertilisers are MgCl$_2$ and Mg(H$_2$PO$_4$)$_2$. However, the high Cl$^-$ concentration of the first makes it applicability as fertiliser limited and, for the second, the P-recovery as from the urine would likely be jeopardised by the PO$_4$ RSF of Mg(H$_2$PO$_4$)$_2$. Similarly, one intrinsic limitation of using Mg(NO$_3$)$_2$ is the RSF of NO$_3^-$ that could offset the urea/NH$_4^+$-N gained from the feed rejection loss. Additionally, the high osmotic pressure of Mg(NO$_3$)$_2$ (i.e. 84 bars at 1 M) would ensure high water flux and urine up-concentration. Non Mg$^{2+}$-based fertilisers could also be used if the ultimate target is urine concentration and N-recovery. However, that is outside the scope of the present work. All chemicals used in this study were reagent grade and purchased from Sigma-Aldrich Australia. Draw and feed solutions were prepared by dissolving the salts in deionised (DI) water.
Table 1 Composition and characteristics of the synthetic (non-hydrolysed) urine feed solution (Udert et al. 2006). *Calculated with OLI System Analyser. ** Based on Udert et al. (Udert et al. 2006).

| Composition      | Concentration [g/L] | Characteristics     |
|------------------|---------------------|---------------------|
| Urea             | 16.2                | pH* 4.51 [-]        |
| NH₄Cl            | 1.80                | Osmotic Pressure* 13.4 [bar] |
| Na₂SO₄ (anhydrous) | 2.30                | Alkalinity** 0.02 [M] |
| NaH₂PO₄ (anhydrous) | 2.90                | Ionic Strength** 0.18 [M] |
| KCl              | 4.20                | TDS* 9.1 [g/L]      |
| NaCl             | 0.18                |                     |

2.2 Forward osmosis experimental set-up

An FO set-up, similar to the one used in our previous study (Phuntsho et al. 2012), was employed in the present research. In particular, for the bench-scale experiments, commercially available thin-film composite (TFC) polyamide (PA) membranes (Toray Chemical Korea Inc., South Korea) were tested. Transport and structural parameters of the FO membranes (A, B and S values) were determined using both traditional pressure driven method (at 8 bars pressure) and the FO method proposed by Tiraferri et al. (Tiraferri et al. 2013). The results are displayed in
Table 2. The crossflow membrane unit consisted of an FO cell with channels dimension of 2.6 cm width x 7.7 cm length x 0.3 cm depth, with an active membrane area of 20.02 cm². The DS tank was placed on a digital scale connected to a computer to record the transported volume. A conductivity and pH meter (Hach, Germany) were connected to the feed tank to record the pH and conductivity of FS. Triplicates of each experiment were conducted.
Table 2 Key properties of the FO membranes and draw solutions used for this study.

|                         | Unit            | TFC             |
|-------------------------|-----------------|-----------------|
| Active layer            | [-]             | Polyamide       |
| Manufacturer            | [-]             | Toray Industry  |
|                         |                 | Inc.            |
| A                       | [L.m².h⁻¹.bar⁻¹] | 6.64            |
| B<sub>NaCl</sub>        | [L.m².h⁻¹]      | 1.17            |
| B<sub>MgSO₄</sub>       | [L.m².h⁻¹]      | 0.91            |
| B<sub>Mg(NO₃)₂</sub>    | [L.m².h⁻¹]      | 3.58            |
| S                       | [μm]            | 409             |
| D<sub>MgSO₄</sub>       | [m².h⁻¹]        | 1.70×10⁻⁶       |
| D<sub>Mg(NO₃)₂</sub>    | [m².h⁻¹]        | 3.31×10⁻⁶       |

2.3 Modelling of water flux, reverse salt flux and achievable P-recovery

To better understand and comment the experimental results, the water flux ($J_w$), specific reverse salt flux (SRSF) have been modelled via the classical solution-diffusion model coupled with the diffusion-convection transport in the membrane support layer (Tang et al. 2010). Membrane pure water permeability ($A$) and the MgSO₄ and Mg(NO₃)₂ salt permeability coefficients (i.e., $B_{MgSO₄}$, $B_{Mg(NO₃)₂}$) were determined via equation 1 based on the corresponding water flux and RO rejection data (at 8 bar pressure) (Zhang et al. 2014). The diffusivity coefficients of MgSO₄ (i.e., $D_{MgSO₄}$) and Mg(NO₃)₂ (i.e., $D_{Mg(NO₃)₂}$) have then been calculated using OLI Stream Analyzer software. The results are displayed in
The impact of the internal concentration polarisation (ICP), on the porous support layer of the FO membrane, needs to be considered to obtain a more realistic theoretical $J_w$ and $J_s$ values. Since all the experiments have been carried out in FO mode (i.e., active layer (AL) facing the feed solution (FS)), equation two was used to predict the water flux (Tang et al. 2010, Zhang et al. 2014).

$$J_w = \sigma K_m \ln \left( \frac{A\pi_D + B_s}{A\pi_F + J_w + B_s} \right) \quad \text{(AL-facing FS)}$$  \hspace{1cm} (2) 

Where $\sigma$ is the reflection coefficient, assumed as unity (complete rejection of the solute), $K_m$ is the mass transfer coefficient, of the selected DS, given by the ratio between the diffusivity of the salt and the structural parameter (S) of the membrane (i.e. $K_m = D/S$). The transport coefficients for water and solutes are expressed as $A$ and $B_s$. Finally, $\pi_D$ and $\pi_F$ are the DS and FS bulk osmotic pressure, respectively. Assuming that the osmotic pressure of the DS follows the van’t Hoff equation, the reverse salt flux ($J_s$) can be calculated using equation 3.

$$J_s = \frac{B_s}{A\beta R \gamma T} J_w$$  \hspace{1cm} (3) 

The specific reverse salt flux (SRSF) can then be calculated as $SRSF = J_s / J_w$.

The theoretical minimum Mg$^{2+}$ dose to precipitate 99%, 90% or 80% of PO$_4^{3-}$ as struvite (ammonium magnesium phosphate hexahydrate = NH$_4$MgPO$_4$.6 H$_2$O was calculated...
assuming Mg\textsuperscript{2+}/PO\textsubscript{4}\textsuperscript{3-} the molar ratio of 1.1 ± 0.1 mol (Etter et al. 2011). In fact, the theoretical molar Mg\textsuperscript{2+}/PO\textsubscript{4}\textsuperscript{3-} the ratio of 1 mol often not enough to achieve a good P-recovery. Given the initial PO\textsubscript{4}\textsuperscript{3-} concentration in the synthetic urine the minimum required Mg\textsuperscript{2+} - SRSF was calculated via equation 4. The variable in this equation is the feed up-concentration factor. The FS concentration factor defines the transported water volume, which determines the amount of Mg\textsuperscript{2+} supplied to the urine during the FO operation.

\[
\text{Minimum required } \frac{Mg^{2+} \text{ - SRSF}}{L} = \frac{(Mg^{2+}_{\text{Required}} - Mg^{2+}_{\text{In urine}})}{1 - \left( \frac{V_{\text{Feed}}}{\text{Feed up-concentration}} \right)}
\]

By substituting the required stoichiometric Mg\textsuperscript{2+} on equation 4 (Mg\textsubscript{Required}) with the amount of magnesium already present in the urine (Mg\textsubscript{In urine}), and considering 1L of urine, the minimum Mg\textsuperscript{2+} - SRSF required to achieve PO\textsubscript{4}\textsuperscript{3-} recovery of 99%, 90% and 80% was calculated. In Figure S2 the minimum Mg\textsuperscript{3+} - SRSF is plotted as a function of the feed up-concentration. From this figure, it can be seen that above 50% FS up-concentration, there is little variation in the required SRSF. That is because after 2 times FS up-concentration already 50% of the volume is moved from the FS to the DS.

### 2.4 Experimental protocol and performance evaluation

Given this required Mg\textsuperscript{2+} - SRSF, short-term experiments, with 1 M MgSO\textsubscript{4} and 1 M Mg(NO\textsubscript{3})\textsubscript{2} as DS and DI water as FS were performed. Water flux and Mg\textsuperscript{2+} - SRSF were measured in each experiment.

For the experiments with synthetic urine as FS, the concentration of MgSO\textsubscript{4} was increased to 2 M to be able to reach at least 50% FS concentration (Figure S1). Also, both FS and DS were acidified to a pH of 4, with a 4 M HCl solution, to avoid precipitation of Mg\textsuperscript{2+} salts on
the surface of the membrane. This acidification step, however, might not be necessary using real fresh urine due to the presence of organic acids (mostly uric acid). Yet, this has to be further investigated. Water flux, urine volume reduction were then recorded by weight measurements. Feed and draw samples were collected over time to measure urea and NH$_3$ rejection as well as the magnesium RSF. After the FO filtration, the pH of the concentrated FS was increased to 9.5, to trigger the mineral precipitation, by slowly adding 4 M NaOH solution. This step is not necessary when real urine is used since the remaining urea in the feed would spontaneously hydrolyse causing pH to rise to 9.5. Afterwards, the FS was then stirred for 2 hours and later filtered using a 0.45 µm pore-size filter (Merck, Millipore).

Additionally, PO$_4^{3-}$ was measured in the feed (1) at the beginning of the experiment (2) after the FO concentration and (3) after mineral precipitation and filtration to calculate the P-recovery.

2.5 Analytical methods

The reverse flux of magnesium was measured using microwave plasma atomic emission spectrometry (MP-AES) (Agilent Technologies, Australia), while sulphate (SO$_4^{2-}$), nitrate (NO$_3^-$) and orthophosphate (PO$_4^{3-}$) anions were measured via ionic chromatography (IC Thermo Fisher Scientific, Australia). The forward flux of ammonium (NH$_4^+$) and urea was measured via spectrophotometer, at 340 nm wavelength, using urea/ammonium Megazime kit. The crystals produced after the FO process were analysed by X-Ray diffraction (XRD) (Siemens D5000), over a Bragg angles ranging from 6° to 60° (Cu Kα, λ=1.54059 Å), and energy-dispersive X-ray spectroscopy (EDX) (Zeiss Supra 55VP, Carl Zeiss AG, Germany). The surface of the scaled membrane was analysed by scanning electron microscopy (SEM, Zeiss Supra 55VP, Carl Zeiss AG, Germany). Samples were firstly dried under air purging.
and then lightly coated with Au/Pd. The SEM imaging was performed at an accelerating voltage of 10 kV at different magnifications and at various points.
3. Results and Discussion

3.1 Magnesium fertilisers screening and performance prediction

As previously discussed, the initial criteria for the selection of suitable DS where that the chosen fertilisers should contain Mg$^{2+}$ in their chemical formula while being fully water-soluble and lacking a phosphate group. Only two fertilisers were selected as DS for this application, i.e., MgSO$_4$ and Mg(NO$_3$)$_2$. Firstly, the osmotic pressure of the two DS was investigated. Between the two, Mg(NO$_3$)$_2$ generates by far the highest osmotic pressure at the same concentration (Figure S1) while having a higher diffusivity coefficient (}
Table 1) (i.e., inducing less dilutive ICP). This means that a concentrated Mg(NO$_3$)$_2$ DS, could potentially achieve greater urine volume reduction with higher water flux compared to MgSO$_4$. The higher water flux was confirmed experimentally (Figure 2). On the other hand, it has to be verified that the RSF of NO$_3$-N from Mg(NO$_3$)$_2$ does not offset the nitrogen recovered from the rejection loss of urea-N/NH$_3$-N. Overall, Mg(NO$_3$)$_2$ showed almost three times the water flux of MgSO$_4$ at same concentrations. Higher SRSF were also measured with Mg(NO$_3$)$_2$, probably due to its higher diffusivity.

After testing the DS with DI water as FS, the experimental results were then used to validate the model described in the previous section. Having a precise model, able to predict the performance of the selected DS, is important when it comes to developing an economic analysis of the FDFO under different operating conditions. By looking at Figure 2, it can be seen that the model shows good agreement with the $J_w$ and SRSF measured during the bench-scale study. Given this good agreement, the developed model was then applied to predict the water flux of long-term tests using fresh urine as FS.
Figure 2. Experimental $J_w$ and SRSF, with 1 M MgSO$_4$ or Mg(NO$_3$)$_2$ as DS and DI-water as FS (columns) are plotted against the $J_w$ and SRSF predicted using equations 2 and 3 (symbols). The input data for the modelling are displayed in
3.2 Experiments with fresh urine as feed solution

Once the model was validated with DI water as FS, long-term tests with fresh synthetic urine were conducted to measure $J_w$, FS up-concentration, $\text{Mg}^{2+}$ - SRSF, P and N recovery data. The DS concentration used for these tests were: 2 M $\text{MgSO}_4$ and 1 M $\text{Mg(NO}_3)_2$. Feed up-concentration of 60% was targeted for both fertilisers.

Starting with the effectiveness of the model when urine is used as FS, Figure 3 shows that the model generally well predicted the $J_w$, especially when $\text{Mg(NO}_3)_2$ is used. However, for $\text{MgSO}_4$, after approximately 40% feed up-concentration the measured flux is higher than the modelled one. A possible explanation is the loss in osmotic pressure of the FS due to the urea movement to the DS, thereby increasing the osmotic pressure difference ($\Delta\pi$) between FS and DS. The loss in osmotic pressure due to urea transport might be particularly evident for $\text{MgSO}_4$ due to its longer experimental time (due to the average lower water flux). Previous findings by Zhang et al. (Zhang et al. 2014) have already noticed this difference between experimental and modelled water flux during concentration of fresh synthetic urine with NaCl as DS. Another explanation could be due to the stripping of $\text{NH}_3$ during the experiment, due to the relatively fast feed recirculation rate (i.e. 300 mL/min). However, ammonia volatilisation should not significantly affect the system since at $\text{pH} \leq 5$, the equilibrium $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$ should be heavily shifted on $\text{NH}_4^+$ which is non-volatile. Besides, the $\text{NH}_3/\text{NH}_4^+$ concentration is relatively low compared to urea. Finally, 60% FS volume reduction was achieved without any sign of membrane damage. In fact, decrease a in the water flux was mainly due to the increase in the osmotic pressure of urine (from about 11-13
bar to around 30 bar) and the decrease in the osmotic pressure of the DS (due to dilution).

Flushing the membrane with DI-water was generally enough to clean the membrane surface and restore the initial performances (Figure S3). Nonetheless, experiments having real urine as FS are necessary to better assess membrane fouling in this process.

Overall, the model showed an acceptable agreement with the measured data and the experimental tests confirmed that at least 60% FS concentration was achievable without any sign of scaling on the membrane.

**Figure 3:** $J_w$ and FS up-concentration factor for the long-term FO experiment using 1 L of synthetic FU as feed and 1 L of 2 M MgSO$_4$ (B) and 1 L of 1 M Mg(NO$_3$_2) (A) as DS.

### 3.3 Mineral phosphorous recovery

Once the targeted FS concentration was reached, the pH of the feed was increased to 9.5 via the addition of a 4 M NaOH solution that resulted in a sudden mineral formation (Xie et al. 2014). The FS was then left to stir at 500 rpm for 2 hours to allow full nucleation and crystals growth. This alkalinisation step expected to be unnecessary when real urine is used. In fact, the enzymatic hydrolysis of urea, which has spontaneously happens in real urine, would itself increase the pH up to 8.5 - 9.5 (Mehta et al. 2015, Randall et al. 2016, Udert et al. 2003). In
this process, the urea concentration after the FDFO process is about the same as in the diluted urine (i.e. 50% urea removal was achieved but also 60% volume reduction). Therefore, it is expected that, after the urea hydrolysation process, the concentrated urine would yield a similar final pH. Phosphorous and magnesium concentrations were measured before and after the alkalinisation of the feed, and the insoluble minerals produced were analysed via XRD and SEM - EDX. Figure 4 shows the amount of $\text{Mg}^{2+}$ and $\text{PO}_4^{3-}$ before and after the mineral precipitation. Both draw solutions achieved around 40% $\text{PO}_4^{3-}$ removal despite the different DS molar concentrations and water fluxes. All the magnesium that diffused through the membrane during the process was removed after precipitation.

Figure 4 Magnesium and phosphorous in the urine before the FO, after the FO and after the NaOH addition in the concentrated urine. Figure 4 (A) refers to the tests with 1 M $\text{Mg(NO}_3\text{)}_2$ and Figure 4 (B) to the ones with 2 M $\text{MgSO}_4$.

After desiccating at room temperature, the solids obtained from the alkalinised FS, SEM - EDX and XRD were used to identify the elemental composition and structure of the crystals. Figure 5 shows the XRD spectrum of the precipitates while Figure 6 the SEM - EDX. In the

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XRD, the peaks of the sample match quite well with the standard peaks of struvite, according to the literature, while the EDX shows that the molar ratio of Mg and P is almost 1:1 (Xie et al. 2014, Xu et al. 2015). The crystals obtained with both fertilisers were identical at the SEM – EDX and XRD spectrum.

Finally, from these results, it can be concluded that almost all the Mg\(^{2+}\) that moved to the FS during the filtration has reacted with the NH\(_{4}^{+}\) and the PO\(_{4}^{3-}\) in the urine to form insoluble struvite crystals. At 60% FS concentration, the RSF of Mg\(^{2+}\) was enough to recover 40% of the PO\(_{4}^{3-}\) in the urine.

Figure 5 XRD spectrum of the precipitates obtained from the concentrated FS after FO filtration. The solution pH was further increased to 9.5 by addition 4 M NaOH. Continuous stirring was applied for two h, and crystals were recovered and dried in a desiccator at room temperature.
Figure 6 SEM picture and EDX spectrum of the precipitates obtained after the filtration of the concentrated urine.

3.4 Nitrogen recovery

Finally, during the experiments, the concentration of urea and NH$_3$ were measured in the DS while NO$_3^-$ in the FS (when Mg(NO$_3$)$_2$ was used as DS). Given the absence of charge and the low molecular weight of urea, it was hypothesize that the FO membrane could not well reject it, thereby leading to an enrichment of the fertiliser DS with extra nitrogen (Cath et al. 2005).

The results, plotted in Figure 7, showed that this hypothesis was, at least partially, correct. In fact, at 60% FS concentration, up to 50% of the urea was recovered in the process. In particular, the flux of urea to the DS was found to be much higher than the RSF of NO$_3^-$ when Mg(NO$_3$)$_2$ was used.
Figure 7 The histograms on the left y-axis show the total amount of urea-N “harvested” from the urine DS and the nitrate –N lost as reverse salt flux. On the right y-axis, the overall complete nitrogen recovery is plotted. Figure 7 (A) refers to the tests with 1 M Mg(NO$_3$)$_2$ and Figure 7 (B) to the ones with 2 M MgSO$_4$.

To conclude, at this stage, not all the P and N in the urine were recovered. However, the process still can be further optimised. For instance, the effect of transmembrane pressure (TMP) in the RSF and urea rejection could also be investigated. Additionally, the performances of real urine should be investigated as it will likely behave differently due to its very heterogeneous concentration. Nonetheless, the simplicity and low cost of the process could incentivise further investigations to reach higher P, N recovery.

4. Conclusions

This study investigated a novel application for FO to concentrate human urine while simultaneously recovering the phosphorous and nitrogen in it. Nitrogen recovery is achieved by urea transport over the FO membrane, enriching the fertiliser draw solution with urea.
Simultaneously, phosphorous recovery is obtained on the feed side of the FO membrane by P-precipitation as struvite due to the RSF of \( \text{Mg}^{2+} \). In this process, the inherent limitations of FO (i.e. RSF and poor urea/NH\(_3\) rejection) are desirable and contribute to the simultaneous recovery of P/N from the urine, while reducing its volume. Process modelling, as well as experimental tests, were used to understand better and critically analyse the results. Two \( \text{Mg}^{2+}\)-fertilisers (i.e., \( \text{MgSO}_4 \) and \( \text{Mg(NO}_3)_2 \)) were identified as the most promising for this application. Among the two \( \text{Mg(NO}_3)_2 \) displayed a much higher water flux and osmotic pressure, achieving equal P and N recoveries as \( \text{MgSO}_4 \). Overall, the FDFO process enables to obtain, simultaneously, the following outcomes:

- Reducing the volume of urine by more than 60% thereby possibly improving the efficiency in downstream processes for N-recovery (e.g. ammonia stripping).
- Recovering 50% of the nitrogen in the urine,
- Recovering 40% of the phosphorous as struvite fertiliser.

To conclude, this low cost and robust treatment process enable a unique way to integrate urine volume reduction and P and N recovery. The economic feasibility of this technology, to produce fertiliser for green walls, parks or urban farming applications, should be further investigated in view of enhancing the sustainability of the urban water cycle.
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Research highlights

- FDFO could be used for simultaneous urine dewatering, urea and phosphorous recovery;
- About 50% of the nitrogen and 40% of the phosphorous were recovered while 60% of urine concentration was reached;
- Phosphorous precipitated as mineral struvite;